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EXPERIMENTAL PROGRAM TO INVESTIGATE STABILITY, COMPATIBILITY AND CORROSION OF POISON SOLUTIONS AND STRUCTURAL MATERIALS

Task 3B

FEASIBILITY OF A CHEMICAL POISON LOOP SYSTEM

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prepared for

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SUMMARY REPORT

EXPERIMENTAL PROGRAM TO INVESTIGATE STABILITY, COMPATIBILITY AND CORROSION OF POISON SOLUTIONS AND STRUCTURAL MATERIALS

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Experimental Program to Investigate Stability, Compatibility and Corrosion of Poison Solutions and Structural Materials

by

D. N. Fultonberg
G. R. Taylor

I. ABSTRACT

31624

The experimental programs and the associated facilities, designed to investigate the compatibility of various combinations of nuclear poison solutions and structural materials, are described. The discussion of the test results and the conclusions drawn are aimed at allowing an assessment of the feasibility of utilizing a Chemical Poison Loop System (CPLS) for the reactivity control of a Tungsten-Water Moderated Rocket Reactor. Reference poison solutions containing cadmium sulfate and reference structural materials of 316 stainless steel and Zircaloy-2 were subjected to low temperature and pressure beaker tests, high temperature and pressure autoclave tests and high temperature and pressure circulating loop tests.

II. SUMMARY

In order to establish the feasibility of utilizing a Chemical Poison Loop System (CPLS) for the reactivity control of a Tungsten-Water Moderated Rocket Reactor (TWMR), a nuclear poison solution and structural materials must be found that would be compatible at the conditions expected during the reactor lifetime. Based upon a literature survey and past experiences, cadmium sulfate solution was chosen as the reference poison with 316 stainless steel and Zircaloy-2 as the reference structural materials.

An experimental program was undertaken by Westinghouse Atomic Power Division, under contract to NASA, Lewis Research Center, to investigate the compatibility between these materials. The program included beaker tests, autoclave tests and circulating loop corrosion tests. Some of the variables examined were temperature, time, solution pH, fluid velocity, heat flux and surface preparation. Structural materials tested were; 304 and 316 stainless steel, Zircaloy 2 and 4, a zirconium-niobium alloy, 6061-T6 aluminum and inconel. The only chemical poison solution tested was cadmium sulfate in demineralized water with sulphuric acid added as required to adjust the pH.

Analyses were performed after completion of a test in order to determine the amount of residue formed, its composition, the solution composition, corrosion of structural materials, and cadmium deposition on these materials.

Some conclusions can be made regarding the solution stability and its compatibility with various structural materials. Among the more significant of these is that the structural integrity of the reference containing materials will be maintained at all conditions tested, due to the relatively low levels of corrosion experienced. The feasibility of using cadmium sulfate as the controlling medium will depend upon the exact nature of the conditions for each application. The stability of the solution is strongly dependent on temperature, and somewhat dependent on surface area of the container relative to fluid volume. The use of cadmium sulfate solution is questionable at temperatures as low as 250-300°F. More extensive tests will be required in order to establish the feasibility of using these materials for chemical poison control.

Deposition of cadmium on container materials also shows some dependence on temperature, fluid velocity and surface to volume ratio. There may also be some dependence on heat flux or on temperature gradients in the container surfaces in contact with the fluid. Additional testing is required for clarification in this area and also to determine the cause of the solution instability.

III. INTRODUCTION

The reference method of reactivity control of the Tungsten-Water Moderated Reactor is accomplished by means of controlling the concentration of a nuclear poisoning material in a solution flowing through the reactor core. The principle of control would be to add sufficient quantities of a high cross section chemical to the system when a reduction in reactivity is required, such as at shutdown, and to remove this chemical when additional reactivity is needed, such as at startup. A feasibility study was undertaken to design and test a system capable of accomplishing these tasks. This system, the Chemical Poison Loop System (CPLS) is shown in schematic form in Figure 1.

The brief system description provided below is included only to help enumerate the conditions to which the chemical solution and containing system will be subjected. More detailed discussions can be found in the feasibility study task reports published by WAPD.[1,2]

> Solution is continually flowing through the primary piping and through the in-core tubes. When poison is required, the solenoid valve in the pressurized poison reservoir is opened, and concentrated poison solution is injected into the primary flow stream until the solution cross-section reaches the desired level. When poison must be removed from the system, the solenoid valve in the ion-exchange line opens, allowing solution to flow through this system and back again to the primary lines. The poison is removed from solution in the exchanger until the solution in the in-core tubes has been reduced in cross section to the desired level. Additional components included a system pressurizer, a main-circulating pump, a loop cooler, a distribution manifold and the required temperature, pressure and flow recording and controlling devices.

It is obvious from examination of the CPLS Flow Diagram Schematic and the brief description, that this system will be subjected to variations in temperature, heat flux, radiation flux, flow rate, and solution concentration. Therefore, the selection of a chemical poison solution and structural materials must be based upon the anticipated limits of these variables and the requirements imposed by NASA in the contract NAS 3-5215 between Lewis Research Center and Westinghouse Electric Corporation, Atomic Power Division.

A survey was first conducted of possible poison solutions, structural materials, and the effect of one upon the other, in order to choose the best combination to be used as a reference for the CPLS. The reference poison solution must meet certain criteria during all periods of containment and these are:

a. Solubility in the required concentration range.

b. Thermal stability.

c. Radiation stability.

d. Suitable nuclear cross-section.

e. Adaptability to removal by ion exchange.

f. Corrosiveness.

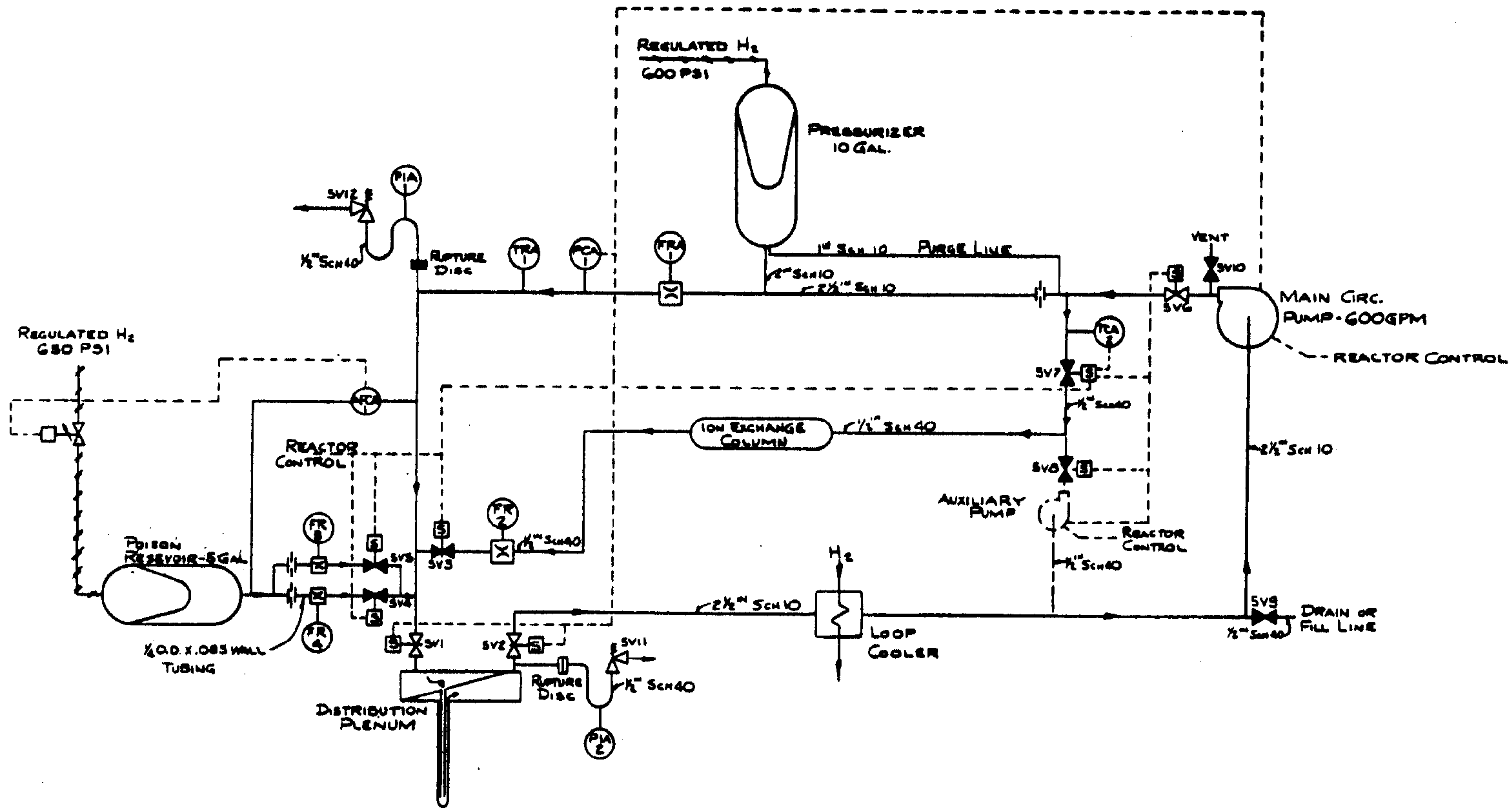


Figure 1

Chemical Poison Loop System
Flow Diagram

The metal chosen as the structural material to contain the poison solution must exhibit the best possible combination of the following properties:

a. High strength at design temperature.

b. Low neutron cross section for in-pile components.

c. Undergo no radiation damage.

d. Compatibility with solution chemistry.

e. Fabricable in the desired shapes.

A complete discussion of the information gathered pertaining to solution and metal properties, resulting from the survey can be found in Section III, A of Reference 1. It will suffice here to say that as a result of the survey, cadmium sulfate was chosen as the reference poison solution, fully understanding that a series of tests of its stability and compatibility would be required in order to establish the feasibility of its use. The backup poison solution was chosen to be boric acid. Its thermal stability and compatibility properties are well known. It was also recommended that in-pile tests be conducted to establish the feasibility of its use in a system with the neutron and gamma flux distribution to be experienced in TWMR. Such testing was specifically outside the scope of the investigation reported herein.

The reference structural materials were chosen to be Zircaloy-2 for the in-core tubes, and 316 stainless steel for all out-of-core components. Tests of these materials under CPLS simulated conditions were required to establish the compatibility with the cadmium sulfate solutions.

IV. REQUIREMENTS OF MATERIALS

Certain requirements have been set forth that must be met by the poison solution, structural material or both, in order to establish the use of chemical poison control for the TWMR. These requirements include:

a. Temperature of operation.

b. Pressure of operation.

c. System nuclear cross section.

d. Concentration of poison in solution.

e. Solution stability.

f. Solution-structure compatibility.

g. Duration of operation and schedule.

h. Material strength.

i. Fluid velocity.

j. Heat flux.

k. Ability to ion exchange for salt removal.

Some of these requirements described below, were established in the contract between NASA and Westinghouse. Others were set forth during discussions between the two parties, or resulted from the flight system design.

a. Temperature of Operation

The maximum temperature of the solution during reactor operation will be 250°F, with a minimum temperature of 60°F. During initial reactor startup and during possible system perturbations, higher temperatures may be operationally desirable; therefore a maximum solution test temperature of 400°F was chosen. The average solution temperature during reactor operation is expected to be about 200°F.

b. Pressure of Operation

The poison system will be pressurized to 600 psia $\pm$ 10 psi during reactor operation. The structural components inside the pressure vessel could experience a pressure differential of approximately 100 psi.

c. System Nuclear Cross Section

The original contract specified nuclear cross section required of the poison solution and structural material during specific reactor operating periods. This was later changed to requirements of poison concentration in solution during these respective periods, rather than cross section. The structural material minimum cross section requirement was modified and it was agreed to design the in-core tubes with a minimum cross section compatible with all other system requirements.

d. Concentration of Poison in Solution

The following list of cadmium concentrations was established based upon the use of cadmium enriched to 90% Cd-113.

Condition	Cadmium, mg/cc	$CdSO_4$, mg/cc
Shutdown	2.97	5.53
Hot Clean	1.65	3.05
Xenon Override	0.126	0.233

It was agreed that all stability and compatibility tests would be operated with cadmium sulfate concentrations 1-1/2 times the shutdown value of 5.53 mg/cc because of the retrograde solubility of this salt and the possibility that the established CPLS concentrations could be changed. The result is that all of the tests described herein were operated with a nominal cadmium sulfate concentration of 8.3 mg/cc.

e. Solution Stability and Compatibility with Structure

The poison solution must be thermally stable at the extreme conditions, as well as average conditions, anticipated during the CPLS lifetime. There were no specific numbers established regarding the allowable instability.

In general, it is necessary that any cadmium deposited in the system not have a serious effect on reactor operation. These effects could be due to the accumulation of cadmium or to a shift of accumulated cadmium from one location to another in the loop. The worst situation appears to be one in which cadmium resulting from instability is deposited in the poison tubes and is then suddenly flushed out of the core region. Preliminary investigations of reactor dynamics were made to estimate limits set by such an accident. These resulted in an estimated allowable deposit of enriched cadmium of 6 $\mu g/cm^2$ of poison tube surface in contact with the solution. The loss of cadmium from solution in the tubes equivalent to uniform deposition of 6 $\mu g/cm^2$ on the tube surfaces is 0.5% of the cadmium initially in an 8.3 mg/cc solution.

Radiation stability determination of the poison solution is necessary, but its investigation was specifically excluded from this program.

The structural integrity of the materials used in the CPLS shall not be adversely affected by the amount of corrosion resulting from exposure to the poison solution during the system lifetime.

Gas generation resulting from corrosion or solution instability must be low enough so as not to appreciably add to the total system pressure or the gas must be removed from the system.

f. Duration of Operation and Schedule

The TWMR is expected to operate for a total of ten hours at full power. This total time will be accumulated during several firings. The control system is expected to startup and shutdown the reactor five times during its operating history. The total elapsed time between firings will be several months. In addition to circulation before and during reactor full power operation, the poison solution will be circulated during shutdown at such a rate as to safely dissipate heat generated in the fluid by gamma heating.

It was agreed upon in discussions between WAPD and NASA, Lewis personnel, that tests be operated for a period of 100 hours. This would be the basis of comparison. Some tests were to be extended for an additional 400 hours to determine the time effect on the results. If test time beyond 100 hours was found to significantly effect feasibility, and time and money permitted, more extended duration tests would then be considered.

g. Material Strength

The structural design must be capable of maintaining a 600 psi pressure. The presence of poison solution should not effect its strength characteristics.

h. Fluid Velocity

The poison solution would be pumped at velocities up to 40 ft/sec during system operation. During extended periods between firings, the solution could be stagnant and therefore zero velocity operation is assumed.

i. Heat Flux

The maximum heat flux across the poison solution control tube wall interface will be 70,000 Btu/hr-ft^2 during operation. In order to be conservative, tests operated during this program were run with a heat flux across this interface of up to 80,000 Btu/hr-ft^2.

j. Ability to Ion Exchange for Poison Salt Removal

Poison salt is to be removed from solution during CPLS operation at least five times by ion exchange. The ion exchange requirements, experimental program and its results will be reported separately.

V. EXPERIMENTAL PROGRAM

The experimental program used to determine the compatibility of the reference poison solution with the reference structural materials is described below. In order to evaluate the performance of these materials under the varied sets of conditions they would be subjected to during the CPLS lifetime, three types of tests were run, namely:

a. Bench or beaker studies.

b. Autoclave tests.

c. Loop studies.

a. Bench or Beaker Studies

These tests were initiated when it was determined they would yield information regarding stability, corrosion, deposition and compatibility, quickly and inexpensively. This would serve the purpose of eliminating certain materials from further consideration at an early date in the program, or at least narrowing down the range of interest for other tests.

The laboratory setup for these tests is shown in Figure 2. It consists of seven, 500 ml Ehrlenmeyer flasks, each fitted with a reflux condenser and positioned on a hot plate. When metallic specimen were being tested, they were suspended in the solution by thin platinum wire. These specimens were all 1 inch by 1-1/2 inches. The respective thicknesses of the materials tested depended upon the availability and varied from 0.125" thickness to 0.030".

Weighed amounts of cadmium sulfate solution of known concentration, pH and resistivity were placed in each flask. The cadmium sulfate used was the reagent grade anhydrous salt obtained from Fisher Scientific Company. Concentrated solutions of the salt were made up and filtered through a 0.45 micron pore size Millipore Filter to remove suspended impurities before diluting to the desired test concentration. The water used to prewash all equipment and for making solutions was first demineralized and in all cases had a maximum conductivity of 0.5 micromho/cm. When pH adjustment of the test solution was required, dilute solutions of reagent grade sulfuric acid or sodium hydroxide, whichever was required, was added to the test flask. A small liquid sample was removed for pH and resistivity measurement. The pH was measured with a silver-chloride probe connected to a Beckman Zeromatic pH meter. The resistivity was measured with a probe connected to an Industrial Instrument Conductivity Bridge. The test flask was reweighed to determine the amount of solution at the beginning of testing. A sample was removed for pH and resistivity measurement rather than measuring directly in the test flask, to prevent possible chloride or silver contamination from the pH probe.

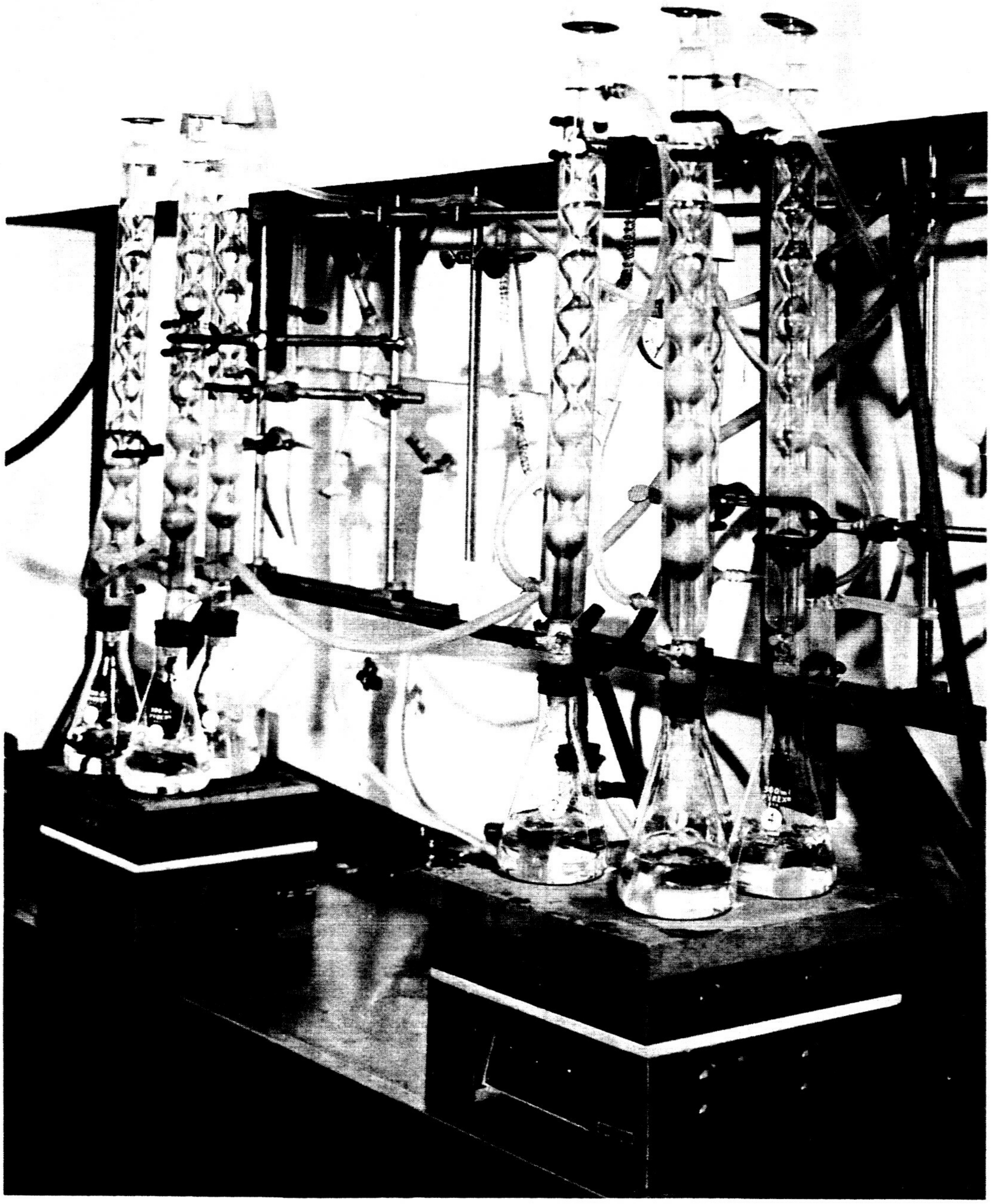


Figure 2 Bench Test Apparatus

Seven of these bench tests were run, each for 100 hours duration. The solution was boiling during this time at a temperature of about 215°F. The test program is shown in Table 1. All numbers are approximate, the exact values being given in the section where test data is listed. Analyses performed to obtain this data will also be described in that same section.

The forty-nine separate flasks run in the seven tests included tests of seven different structural materials and three different rubber materials. Some of the flasks contained nothing but solution.

The thermal stability tests, those with only solution in the flask, were run to determine the effect of heat and solution chemistry on the stability of cadmium sulfate in water solution. Most of these tests were conducted with solutions containing about 8.3 mg of cadmium sulfate per cc of solution. The pretest solution pH range of interest was 1 through 7, and had been adjusted from its natural value of about 5.5-6 using the sulfuric acid or sodium hydroxide where appropriate. A few flasks, in Bench Test #7, had solution containing 300 mg of cadmium sulfate per cc of solution. It was deemed desirable to check the stability of this solution which represented the CPLS poison concentrate tank conditions.

The tests run to establish corrosion, deposition, and compatibility were the same as the stability tests with the exception of the coupons that were suspended in solution. The structural materials tested included 316 stainless steel, 347 stainless steel, 6061-T6 aluminum, Zircaloy-2, Zircaloy-4, zirconium-2.5 niobium and inconel. The 316 stainless steel, aluminum, and the three zirconium alloys were being considered for use in the CPLS and were included in these tests for this reason. The 347 stainless steel and inconel were tested to check the feasibility of using autoclaves fabricated from these materials, during the next phase of testing.

The three types of rubber specimens included in Bench Test #7 were high temperature Buna-N, low temperature Buna-N, and a silicon rubber. These materials were under consideration for use as the bladder material for the CPLS pressurizer-accumulator and the poison concentrate tank.

The information that could be gathered from a series of tests such as this include:

1. Change of cadmium concentration in solution.
2. Amount and composition of residues.
3. Corrosion of structural materials and the resulting hydrogen generation.
4. Effects of solution chemistry.
5. Deposition of cadmium on coupon surfaces.

Table 1

Bench Test Program

Test	$CdSO_4$ conc., mg/cc	No. of Flasks	Solution pH	Coupon Material
1	8.3	6	2 thru 7	316 + 347 SST
		1	6	None
2	8.3	6	2 thru 7	Zirc 2 and Zirc 4
		1	6	None
3	8.3	6	2 thru 7	6061-T6 Alum.
		1	6	None
4	8.3	7	2 thru 7	None
5	8.3	3	2, 3 and 6	Inconel
		4	2 thru 5	None
6	8.3	6	1 thru 6	Zirc 2, Zirc 4 and Zirc-N6
		1	6	None
7	8.3	2	4, 6	High and Low T Buna-N, Silicon Rubber, 316 SST, Zirc 2 and Zirc 4.
	300	2	4, 5	Same
	8.3	1	6	None
	300	2	4, 5	None

b. Autoclave Tests

Autoclave studies were conducted to determine the compatibility of cadmium sulfate solutions with structural materials of interest for use in the CPLS. Among the factors that could be determined by a series of tests of this type include all of those discussed in the Bench Test program plus the effect of temperature.

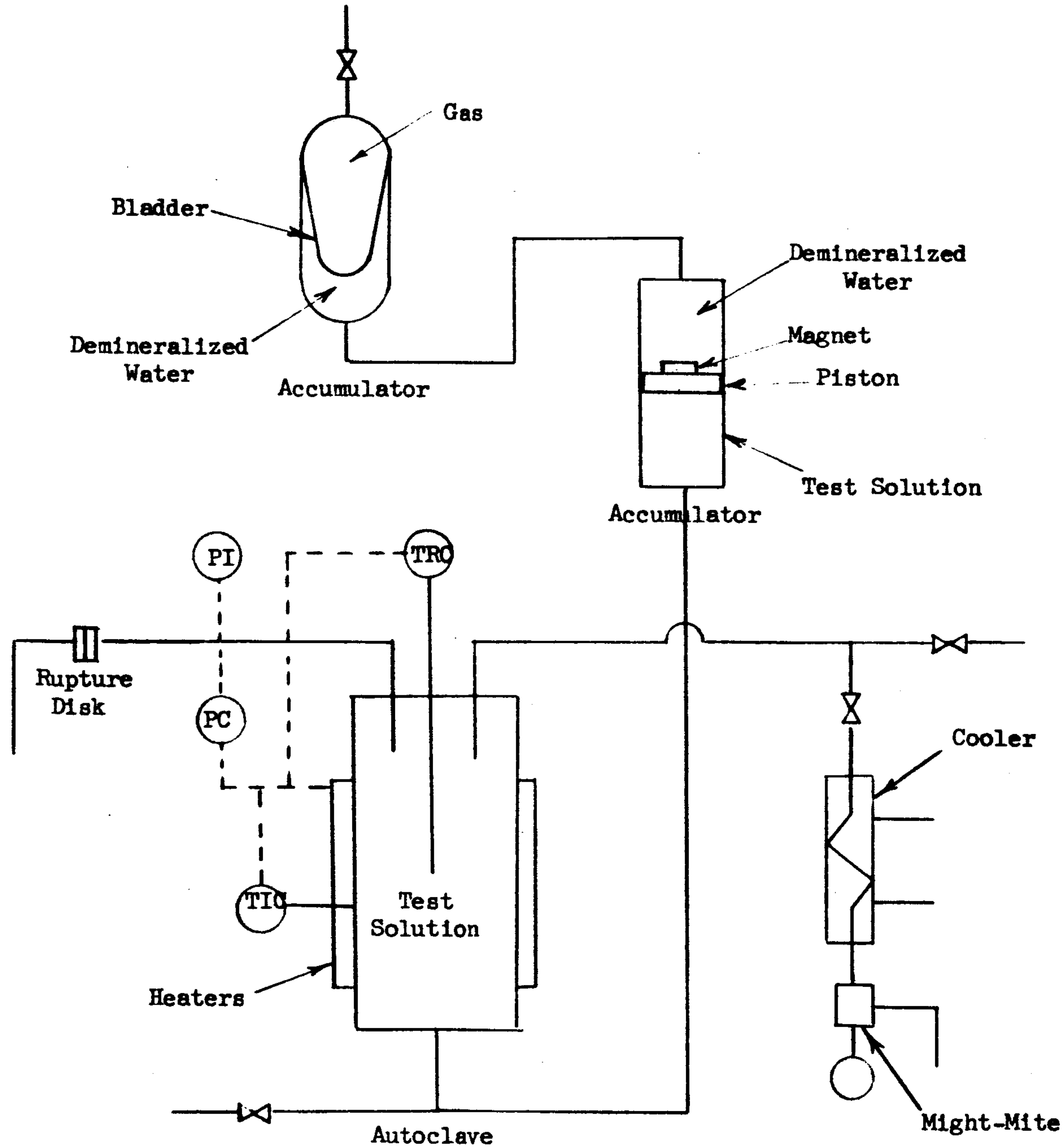
1) Autoclave Facility - Initial plans were made to run these tests in small inconel and 347 stainless steel autoclaves, each with a volume of 18 ml. However, these plans were changed when it was found that the heads of these autoclaves could not be sealed properly. In addition, the "inert" coating applied to the autoclave internals proved to be unstable at test conditions.

Two larger autoclaves, fabricated out of 316 stainless steel, were made available for the program. One autoclave has a 5 inch inside diameter and is 21 inches long, while the other is 14 inches long with the same inside diameter. Associated with each autoclave is a Minneapolis Honneywell Brown Pyrovane connected to a 316 stainless steel clad thermocouple immersed in the test solution. This controls the solution temperature which is also recorded on a 12 point Honeywell Brown Electronik Recorder. The autoclave wall temperature is protected by a Wheelco High Temperature Limit Controller connected to a thermocouple positioned between the strap-on heaters and the outer surface of the wall. This limit controller trips the autoclave heaters and sets off an alarm if its pre-set limit is reached.

All of the tests run during this phase of the program were operated at 600 psi pressure. The control of this pressure varied depending upon the particular test. For those tests which had a liquid-gas interface in the autoclave, the 600 psi was maintained by attaching a bottle of Argon to the system which was fitted with a pre-set bottle regulator. Other tests were run in which the autoclave and all lines to the autoclave were filled with solution and there was no gas present in this primary system. A Hydrodyne Industries Floating Piston Accumulator and a Greer Bladder Type Accumulator were used to control the pressure. A schematic diagram of this setup is shown in Figure 3. The piston in the accumulator was fitted with a magnet on its secondary side. This permitted determination of piston position during operation. The secondary side of the piston accumulator and the primary side of the bladder unit were filled with demineralized water. Argon was added to the bladder to a pressure of 600 psi with the piston in a central position, at the beginning of a test.

Figure 3

Autoclave Test Facility Schematic



Each autoclave was protected from being subjected to excessive pressure by a Meletron Bourdon Type Pressure Switch which trips the autoclave heaters and alarms if a pre-set high pressure is reached. A rupture disk is installed in each system to burst and relieve the pressure if the other safety features fail to control. The pressure in the primary system is indicated by a gauge.

2) Test Program - The tests run in this phase of the program are shown in Table 2. The program was changed and added to as results from previous tests were made available. All of this will be discussed in detail in later sections of the report. The initial solution compositions shown are nominal values. The initial solution pH of tests 3 and 5 were adjusted with sulfuric acid. All other test solutions were at their natural pH, the differences resulting from slightly different compositions of separate batches of cadmium sulfate salt.

Tests 1, 2 and 3 were operated with a liquid gas interface in the system. All others were run with the system filled with test solution, free of any gas. Coupons of 304 and 316 stainless steel, Zircaloy-2 and 4, and zirconium-2.5% niobium alloy were included in all tests except number 2. The specimens were examined to obtain data regarding corrosion rates and therefore hydrogen generation rates, and cadmium deposition on their respective surfaces.

The autoclaves, which are 316 stainless steel, were prepared for testing in different manners depending upon the test requirements. For tests 1, 2 and 3 the internals were wiped clean using alcohol as the cleaning agent to remove any loosely adhering crud from prior testing. In addition, before running the first tests in this program, the autoclaves were filled with demineralized water and boiled to atmospheric pressure. Samples of this water were then analyzed for crud content, pH and conductivity in order to firmly establish the cleanliness of the internal surface. Prior to starting tests 4, 5, 6 and 7, the autoclave internals were cleaned by the alkaline permanganate-citrate cleaning method and rinsed thoroughly with demineralized water. This was done to insure that the surfaces were completely free of any residues or oxide film formed during previous tests.

The alkaline permanganate-citrate cleaning method consists of heating the autoclave to 210°F with a solution containing 10 weight percent sodium hydroxide and 3 weight percent potassium permanganate, the remainder being demineralized

Table 2

Autoclave Test Program

Test No.	Pressure, psig	Temperature, $^{\circ}F$	Initial Cd conc, mg/cc	Initial Solution pH	Test Duration, hr	Specimen Material	Mode of Operation	Surface Condition
1	600	400	8.3	5.9	100	(a)	(d)	(f)
1a	600	400	8.3	5.9	500	(a)	(d)	(f)
2	600	350	8.3	5.9	100	None	(d)	(f)
3	600	350	8.3	3.4	100	(a)	(d)	(f)
3a	600	350	8.3	3.4	500	(a)	(d)	(f)
4	600	350	8.3	5.3	100	(b)	(e)	(g)
5	600	350	8.3	4.1	100	(b)	(e)	(g)
6	600	300	8.3	5.5	100	(c)	(e)	(g)
7	600	250	8.3	5.4	100	(c)	(e)	(g)
8	600	300	8.3	5.4	100	(c)	(e)	(h)
9	600	300	8.3	5.4	100	(c)	(e)	(i)

(a) Measured and weighed coupons of 304 SST, 316 SST, Zirc-2, Zirc-4 and Zirc-nb.

(b) Materials and areas same as (a) but specimens not weighed.

(c) Materials and areas same as (a) but only a few were weighed.

(d) Liquid-gas interface in autoclave.

(e) Autoclave completely filled with liquid, no gas present.

(f) Autoclave surface not prepared special, just wiped clean.

(g) Internal surfaces precleansed by alkaline permanganate-citrate method.

(h) Internal surfaces cleaned before previous test.

(i) Internal surfaces passivated by 750°F, 1500 psi steam.

water. This temperature is maintained for 90 minutes after which the system is drained and filled with boiling demineralized water which is kept boiling for 1/2 hour. The water is drained and replaced by a solution containing 10 weight percent dibasic ammonium citrate in demineralized water which is boiled for two hours. The system was again rinsed with boiling water for 1/2 hour then rinsed with acetone and then alcohol.

The autoclave used for test number 8 had been used for test number 6, before which it had undergone the cleaning method just described. It was not cleaned by this method prior to test 8. Its interior was just rinsed with water and wiped with alcohol.

Test number 9 was run in an autoclave that had been used for test 7 then operated for a few days at 750°F and 1500 psi to form a protective oxide film on all interior surfaces. During this passivation treatment the autoclave was filled with steam.

All of the tests except 1 and 3 were operated for 100 hours. These two were operated for a total duration of 500 hours, but the tests were interrupted after 100 hours in order to remove some specimens, add others, and also take a small amount of liquid for chemical analysis. Therefore, these two tests are shown as 1 and 1a, and 3 and 3a respectively.

As shown in Table 2, the test temperature varied between 200 and 400°F. In addition to this variation, other factors which were changed from test to test were: the duration, solution chemistry, mode of test operation, and condition of metallic surfaces.

c. Loop Studies

The bench tests and autoclave tests covered the range of solution chemistries, structural materials, and temperatures anticipated in the CPLS. However, the effects of two important parameters on solution stability and compatibility could not be examined without more sophisticated testing. These parameters are heat flux and fluid flow, and along with all other factors influencing CPLS feasibility from a materials standpoint, their effects were examined in the pumped loop studies to be described below.

The objectives of these tests were:

a) Determine the deposition of cadmium (hideout) on Zircaloy and 316 stainless steel specimens as a function of: (1) heat flux, (2) fluid velocity, (3) temperature, (4) time and (5) solution chemistry.

b) Determine the corrosion of Zircaloy and 316 stainless steel as a function of the above mentioned variables covering the anticipated CPLS conditions.

c) Determine the stability of cadmium sulfate solution as a function of (1) temperature, (2) time and (3) solution chemistry.

This series of tests was conducted in the Materials Compatibility Test Facility shown in Figure 4. Its instrument console is shown in Figure 5. Figure 6 depicts the schematic diagram of the loop.

1) <u>Loop Design</u> - The materials corrosion loop system will operate at the following conditions:

Maximum Loop Fluid Temperature	$500^{\circ}F$
Maximum Loop Fluid Pressure	600 - 800 psia
Average Loop Flow Rate	10.7 gpm

The primary system consists of loop piping, a pump, a test section, an evaporative cooler, a heater section, and a variable area coupon specimen holder. Auxiliary systems consist of a makeup and letdown system, a purification and decontamination system and additional provisions for hydrogen gas and chemical addition. Provision has been made for the addition of radio-tracer isotopes.

The loop primary piping is 1" Sch. 40 Grade 316H stainless steel rated for $650^{\circ}F$ at 2500 psig. The loop pump, a Chempump Model CFH 1-1/2-3/4S, rated at $500^{\circ}F$ and 2000 psi, developing 92.3 ft. of head at 10 gpm flow will be used to meet the program test section flow requirements.

Immersion heaters, 9 Kw capacity and housed in a 3" Sch. 160, 316H stainless steel pipe assembly provide loop heat requirements. The immersion heater assembly is located on the suction side of the loop pump.

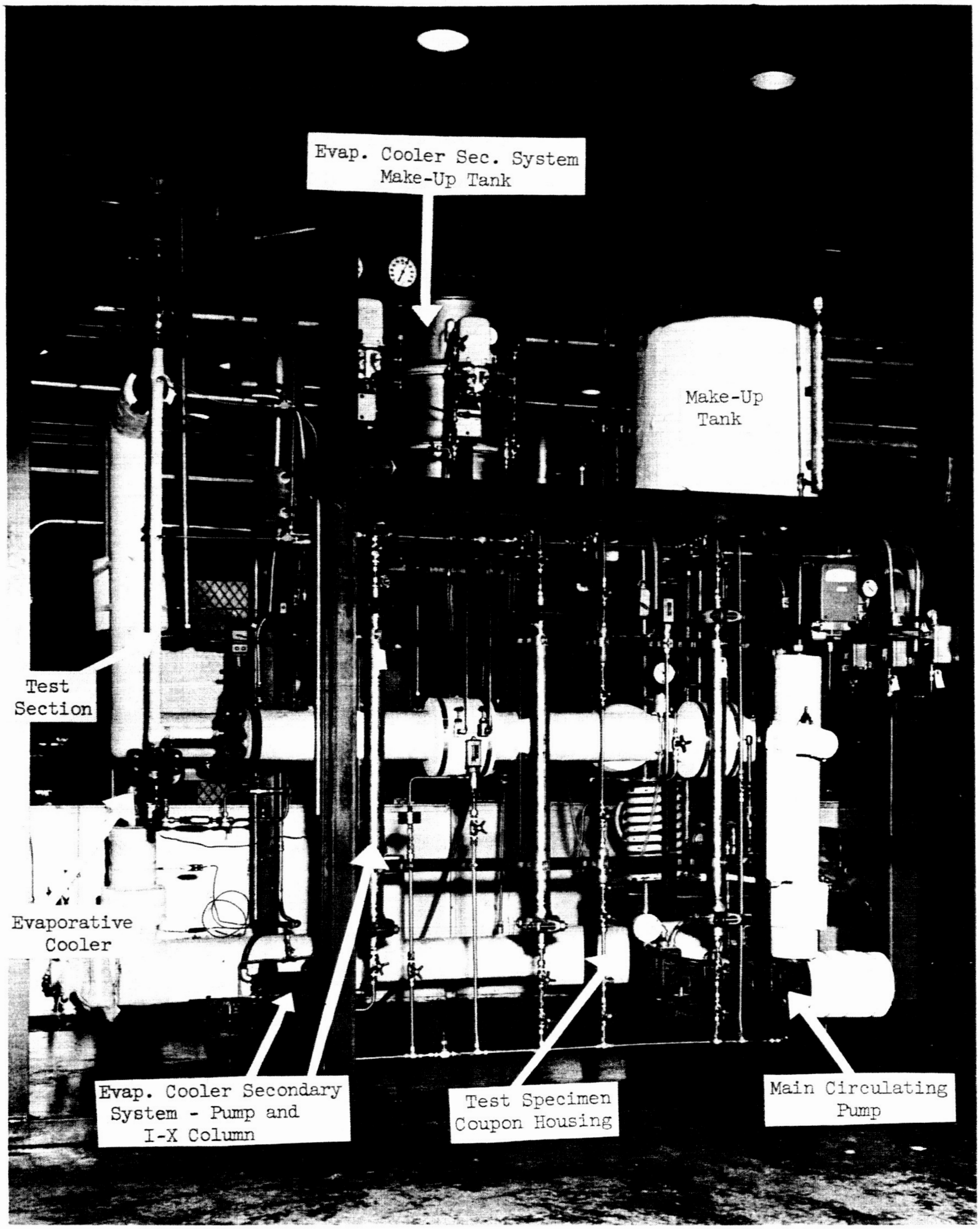


Figure 4 Materials Compatibility Test Facility

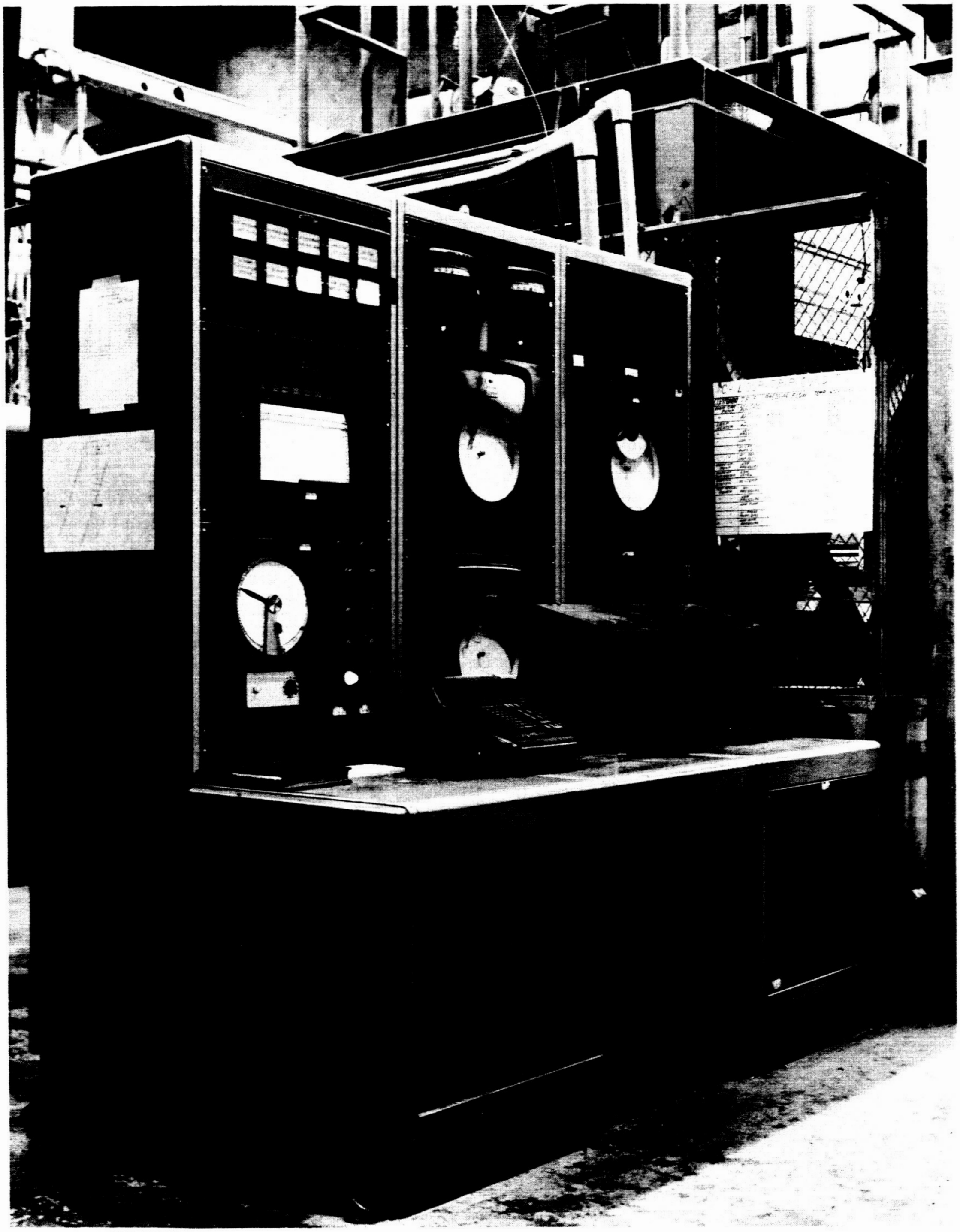


Figure 5 Materials Compatibility Test Loop Control Console

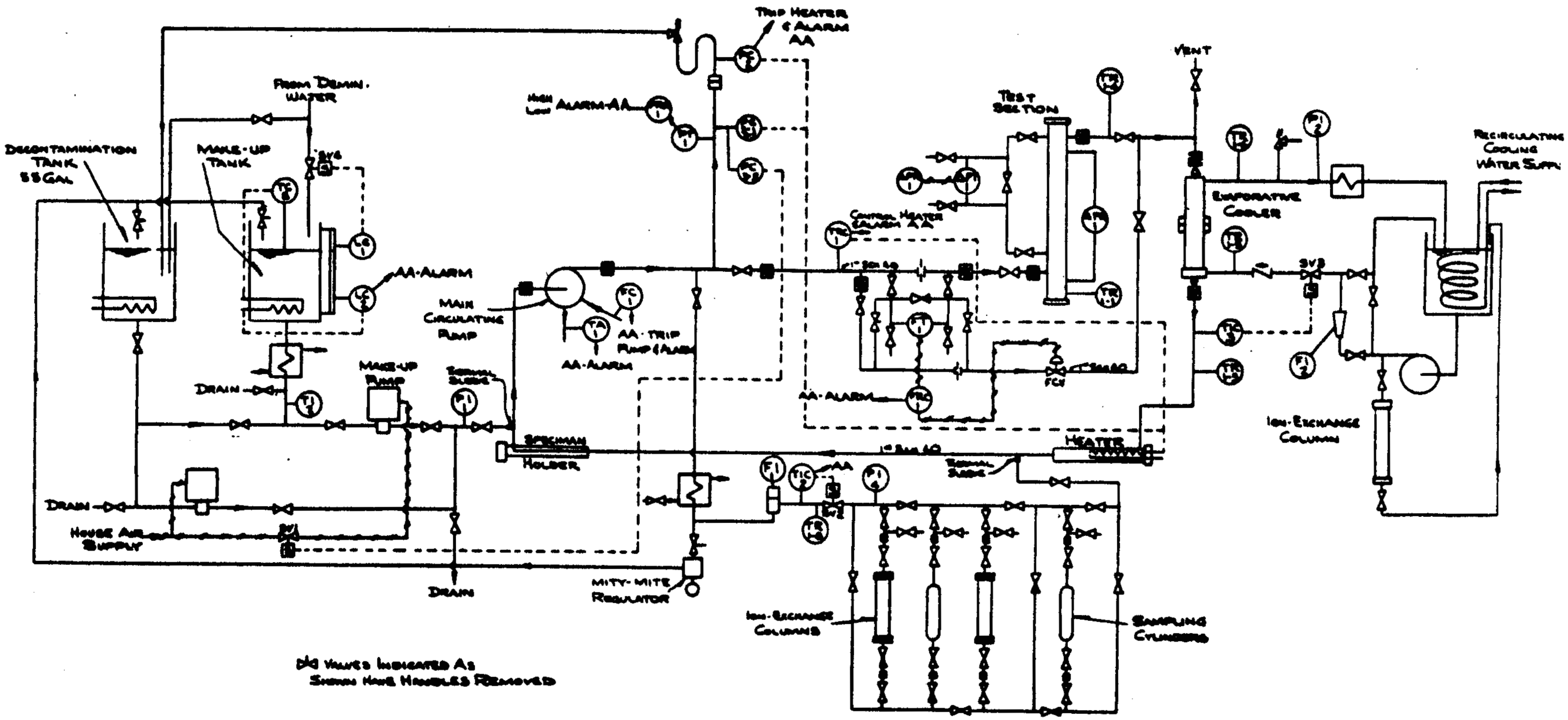


Figure 6

Materials Compatibility Test Loop Schematic

An evaporative cooler with a capacity of 88 Kw, removes test section heat input to the loop fluid. The cooler is fabricated of 2 inch Sch. 80 Inconel pipe, as the primary, with a 3 inch Sch. 5, 304 SS pipe for the secondary cooling water housing.

A section of 3" Sch. 160, 316H stainless steel pipe is located on the suction side of the loop circulating pump and contains a specimen fixture machined to provide a variable area (flow areas 0.1 in.^{2} to 0.7 in.^{2}) along its length and velocities of 5 ft/sec to 35 ft/sec.

The loop purification system consists of a valve rack and two ion exchange columns (2" Sch. 80, 304 SS pipe with Grayloc connections at one end), and can be operated in series or in parallel. Two sampling cylinders for system sampling are provided with tees for H_2 gas or chemical (H_2SO_4, H_3BO_4, $CdSO_4$) addition.

The makeup system consists of one 55 gallon drum with a 10 Kw immersion heater feeding a Sprague makeup pump with an approximate makeup capacity of 53.4 gph at 750 psig discharge pressure. System letdown is accomplished through a letdown cooler to a Grove back pressure regulator relieving at pressures between 100-3000 psia.

A decontamination system has been included to clean the loop, if required, and is in parallel with the existing makeup system. It contains a 55 gallon drum with a 5 Kw immersion heater feeding a Sprague makeup pump with a capacity of 53.4 gph at 750 psig discharge pressure.

Test section power supply requirements have been set at 10-12 Kw based on a heat flux of 80,000 $\frac{\text{Btu}}{\text{hr-ft}^2}$ at the heater test section sheath. Test section power control will use a 220 V, 1 phase powerstat.

2) <u>Test Specimens</u> - There were two types of specimens tested in the loop. The materials being subjected to a heat flux are small right circular cylinders, 0.815" O.D. by 0.035" wall thickness and are 1/2" long each. They are mounted on an aluminum clad, Watlow "Firerod", cartridge type heater which is supported vertically in the test specimen housing as shown in Figure 7. Aluminum was chosen as the heater clad material because of its high coefficient of thermal expansion as compared to 316 stainless steel and the zirconium alloys. The aluminum was treated by the Alumilite Process prior to insertion in the loop to prevent reaction with the cadmium sulfate solution or the test

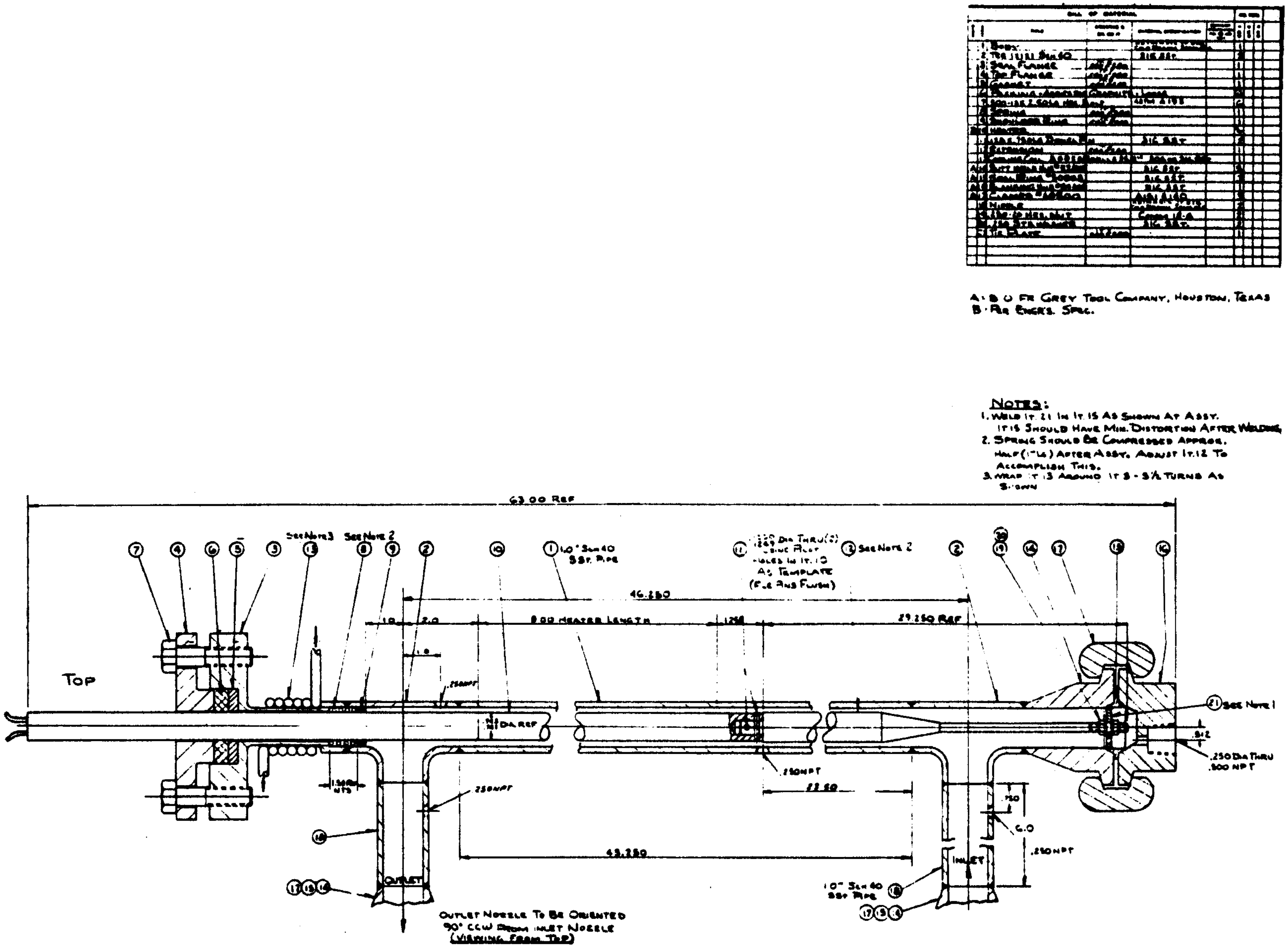


Figure 7

Specimen Housing

specimens. The heater outside diameter and the specimens inside diameters were closely controlled to result in an interference fit at operating temperatures. The specimens are spring loaded on the heater to prevent chattering while the fluid is flowing, before the system is heated to test conditions.

The heater and therefore the specimens are positioned both vertically and diametrically within the housing, by the bottom extension rod which is screwed into the heater end cap at one end and bolted to a plate at the bottom end of the housing. This extension rod also serves to establish well-developed fluid flow characteristics by the time the solution reaches the specimens. The heater which has both electrical leads at its top end, emerges from the housing at the top through a packing gland. The gland seals against the anticipated 600 psi loop pressure but will allow the heater to grow vertically due to its thermal expansion when heated, without buckling.

The specimens tested under heat flux conditions included 316 stainless steel, Zircaloy-2 and Zircaloy-4 alloys. All of these specimens were checked dimensionally and weighed prior to test.

The second type of specimens to be tested in the loop were flat rectangular coupons of 316 stainless steel, 304 stainless steel, Zircaloy-2, Zircaloy-4, and zirconium-niobium alloy. These coupons were immersed in the flowing fluid and were subjected to the bulk fluid test temperatures without any heat flux. The pre- and post-test examinations are similar to those for the cylindrical specimens. The coupons, which are 0.035" thick and have an area exposed to solution of about 1 square inch, are positioned in the loop by a coupon holder. An insert was added to the holder to reduce the cross sectional flow area so that the fluid velocity varied from 5 ft/sec to 35 ft/sec from inlet to outlet of the holder.

3) <u>Test Program</u> - The original program included three loop tests. However, the results of the first test, coupled with autoclave test results, both of which will be discussed later in this report, indicated that unless major changes were made to the operating test conditions, similar results could be expected from the two remaining tests in the program. Therefore, only one test, shown in Table 3, was run.

Table 3

Loop Study Program

Fluid Temp, °F	350
Test Duration, hrs.	90
Heat Flux, Btu/hr-ft^2 °F	75,000
Fluid Velocity, ft/sec	
a) in heater section	10
b) in coupon holder	5-30
$CdSO_4$ conc., mg/cc	8.3
Solution pH	3.
System pressure, psig	600

VI. EXPERIMENTAL RESULTS

A. Bench Tests

The data collected from the seven bench tests are shown in Tables 4 through 10. Bench Test #1 solutions were not analyzed as completely as the remaining tests because test and analytical procedures were being experimented with in this first test. Solution analyses accurately performed included initial and final pH, initial cadmium concentration, weight of residue, cadmium on the flask walls after solution is removed and cadmium in the residue. Subsequent tests also included accurate analyses for initial and final solution resistivity and final cadmium concentration.

Cadmium in solution was determined by flame analysis using a Beckman Instrument, AD Spectrophotometer. Standard solutions containing known amounts of cadmium were checked against the calibration curves each time a sample was being analyzed.

Cadmium in residues and on the surface of metallic specimens was determined by X-ray fluorescence. Both residue and metallic standards of each material being studied were first prepared and used as a check each time analyses were being performed.

The metallic specimens included in most of the tests were weighed before and after test on a Micro Grams-Atic Balance. They were also dimensionally measured to determine surface area. The deposition of cadmium on the specimen surface was analyzed by X-ray fluorescence as described above.

Some of the rubber specimens from bench test #7 were also mechanically tested to compare the elasticity after test with untested specimens.

B. Autoclave Tests

Nine autoclave tests were conducted, some of the variables being test temperature and time, solution pH, mode of test operation and condition of metallic surfaces. The data gathered from these tests are shown in Tables 11 through 14. The analyses performed included pH measurement, cadmium flame analysis, weighings of residues and coupons where applicable, spectrographic analysis of residues and filtrates, cadmium deposition on coupon surfaces by X-ray fluroescence, and coupon stripping of certain stainless steel specimens. The coupon stripping, to determine total metal attack, was performed by the alkaline permanganate-citrate method previously described until there was a constant specimen weight loss. Blank specimens were run simultaneously as checks.

Table 4

Results of Bench Test #1

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	2.03	2.97	4.00	5.01	6.02	6.98	6.02
Final pH	2.08	3.09	3.49	3.98	6.97	6.98	6.84
Initial Resistivity, ohm-cm	Not Taken						
Final Resistivity, ohm-cm	Not Taken						
Initial Cd Concentration, mg/cc	3.80	3.80	3.80	3.80	3.80	3.80	3.80
Final Cd Concentration, mg/cc	Not Accurately Checked						
Total Weight of Residue, mgs /1	2.0	3.8	7.7	8.3	4.3	1.6	3.1
Material Balance for Cd, mgs							
Cd in Solution Initially	952	953	945	946	947	947	938
Cd in Solution Final	Not Accurately Checked						
Cd Obtained from Flask Walls /2	2.9	3.7	3.3	1.7	6.0	9.2	4.3
Cd in Solution Precipitate	0.1	0.1	<0.1	<0.1	2.0	0.2	0.7
Cd Deposited on Specimens	0.1	<0.1	<0.1	<0.1	<0.1	0.2	-
Cd Unaccounted for	No Check						
Specimens							
Material (1)	316 SST-1	316-2	316-3	316-4	316-5	316-6	-
(2)	347 SST-1	347-2	347-3	347-4	347-5	347-6	-
Change in Weight, $\mu g/cm^2$ (1)	-198.8	+1.91	+10.44	+4.98	+13.91	+263.8	-
(2)	-795.0	-1.74	+6.68	+5.19	+18.97	+147.7	-
Cd Depos. on Specimens, $\mu g/cm^2$ (1)	1.6	<0.2	<0.2	1.5	1.5	1.0	-
(2)	4.9	<0.2	1.0	<0.2	2.9	14.0	-

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flask with water.

Table 5

Results of Bench Test #2

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	1.97	2.90	3.98	4.98	6.03	7.03	5.94
Final pH	1.95	3.00	4.20	6.45	6.50	6.60	6.20
Initial Resistivity, ohm-cm	109	250	283	287	290	305	292
Final Resistivity, ohm-cm	108	248	252	258	260	268	262
Initial Cd Concentration, mg/cc	3.868	3.870	3.875	3.896	3.900	3.900	3.900
Final Cd Concentration, mg/cc	3.741	3.748	3.759	3.825	3.707	3.624	3.950
Total Weight of Residue, mgs/1	1.0	0.8	0.8	0.6	1.2	0.6	0.8
Material Balance for Cd, mgs							
Cd in Solution Initially	1011.4	1006.3	1009.9	1005.6	1007.8	995.3	1004.3
Cd in Solution Final	976.5	974.4	972.2	986.9	957.8	924.7	1017.2
Cd Obtained from Flask Walls/2	8.5	8.3	9.3	9.5	16.5	11.7	11.9
Cd in Solution Precipitate	<0.1	0.2	0.1	0.2	0.6	0.3	0.2
Cd Deposited on Specimens	0.1	0.1	0.1	0.2	0.1	0.1	-
Cd Unaccounted for	26.2	23.3	28.2	8.8	32.8	58.5	+25.0
Specimens							
Material (1)	Zirc 2-1	Zirc 2-2	Zirc 2-3	Zirc 2-4	Zirc 2-6	Zirc 2-5	-
(2)	Zirc 4-11	Zirc 4-12	Zirc 4-14	Zirc 4-25	Zirc 4-42	Zirc 4-38	-
Change in Weight, $\mu g/cm^2$ (1)	+1.70	+1.47	+2.05	+8.89	+8.80	+2.98	-
(2)	+0.83	+0.53	-0.30	+9.32	+0.46	+3.58	-
Cd Deposited on Specimens, $\mu g/cm^2$ (1)	5.9	3.5	4.2	8.0	5.4	5.5	-
(2)	<0.2	<0.2	<0.2	0.4	<0.2	1.4	-

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flask with water.

Table 6

Results of Bench Test #3

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	2.00	2.95	4.00	4.95	5.85	7.05	5.90
Final pH	3.91	4.05	4.09	4.18	3.68	4.05	6.89
Initial Resistivity, ohm-cm	105	250	288	290	293	292	293
Final Resistivity, ohm-cm	455	540	535	285	280	285	288
Initial Cd Concentration, mg/cc	3.813	3.819	3.824	3.849	3.850	3.850	3.850
Final Cd Concentration, mg/cc	0.226	0.240	0.263	3.330	3.443	3.734	3.983
Total Weight of Residue, mgs/1	2264	1847	1724	147.0	124.5	13.5	0.9
Material Balance for Cd, mgs							
Cd in Solution Initially	1044.1	1040.0	1041.7	1043.8	1045.7	1046.0	1049.1
Cd in Solution Final	61.1	64.6	70.7	890.9	919.3	1001.7	1070.1
Cd Obtained from Flask Walls/2	39.9	25.7	37.7	17.6	35.6	26.2	12.0
Cd in Solution Precipitate	377.1	342.1	288.0	23.0	24.0	2.1	0.9
Cd Deposited on Specimens	0.4	1.4	0.4	1.5	2.7	2.4	-
Cd Unaccounted for	565.6	606.2	644.9	110.8	64.1	13.6	+33.9
Specimens							
Material (1)	6061-T6A1-1	-T6A1-2	-T6A1-3	-T6A1-4	-T6A1-5	-T6A1-6	-
Change in Weight, $\mu g/cm^2$ (1)	-24,108	-14,101	-8,461	+423.2	-444.9	+745.2	-
Cd Deposited on Specimens, $\mu g/cm^2$ (1)	15.0	56.9	17.7	64.1	114	98.6	-

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flask with water.

Table 7

Results of Bench Test #4

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	1.98	2.88	3.94	4.83	5.86	6.56	7.01
Final pH	2.02	2.88	4.08	6.25	6.41	6.60	6.68
Initial Resistivity, ohm-cm	105	250	288	290	292	295	292
Final Resistivity, ohm-cm	108	265	302	304	310	308	309
Initial Cd Concentration, mg/cc	3.790	3.795	3.802	3.824	3.825	3.825	3.825
Final Cd Concentration, mg/cc	3.689	3.719	3.784	3.857	3.837	3.868	3.844
Total Weight of Residue, mgs/1	0.9	1.1	1.2	0.2	0.2	0.2	0.2
Material Balance for Cd, mgs							
Cd in Solution Initially	993.6	1006.7	988.4	976.6	955.1	942.9	978.8
Cd in Solution Final	957.3	979.1	975.8	976.7	950.7	943.8	976.1
Cd Obtained from Flask Walls/2	4.7	3.5	3.6	5.4	2.8	3.3	3.1
Cd in Solution Precipitate	0.1	0.1	<0.1	0.1	0.1	<0.1	0.1
Cd Deposited on Specimens	-	-	-	-	-	-	-
Cd Unaccounted for	31.5	26.0	8.9	+5.6	1.5	+4.3	+0.5
Specimens	No Specimens						

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flask with water.

Table 8

Results of Bench Test #5

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	1.87	2.80	3.91	5.10	5.78	1.86	2.80
Final pH	1.95	2.60	3.85	6.28	6.40	1.59	2.57
Initial Resistivity, ohm-cm	103	231	262	265	266	103	231
Final Resistivity, ohm-cm	162	250	281	283	283	110	250
Initial Cd Concentration, mg/cc	4.479	4.475	4.486	4.514	4.515	4.476	4.482
Final Cd Concentration, mg/cc	4.504	4.406	4.445	4.496	4.506	4.284	4.454
Total Weight of Residue, mgs/1	0.3	1.2	1.3	0.8	0.4	0.8	0.5
Material Balance for Cd, mgs							
Cd in Solution Initially	1183.4	1164.3	1194.9	1135.2	1145.5	1153.1	1166.3
Cd in Solution Final	1175.9	1132.3	1170.0	1121.2	1131.0	1090.2	1150.4
Cd Obtained from Flask Walls/2	3.0	3.1	3.3	3.2	3.1	3.0	2.5
Cd in Solution Precipitate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd Deposited on Specimens	0.1	<0.1	-	-	0.1	-	-
Cd Unaccounted for	4.3	28.7	21.5	10.7	11.2	59.8	13.3
Specimens							
Material (1)	Inconel-1	Inconel-2	None	None	Inconel-3	None	None
Change in Weight, $\mu g/cm^2$ (1)	-4982	-59.3	-	-	+25.4	-	-
Cd Deposited on Specimens, $\mu g/cm^2$ (1)	2.5	1.5	-	-	2.8	-	-

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flask with water.

Table 9

Results of Bench Test #6

Flask #	1	2	3	4	5	6	7
Solution							
Initial pH	1.00	1.70	2.60	3.75	4.91	5.79	5.79
Final pH	0.89	1.28	1.48	3.72	5.41	5.82	5.88
Initial Resistivity, ohm-cm	33	108	228	257	261	265	265
Final Resistivity, ohm-cm	36.5	108	245	270	285	283	282
Initial Cd Concentration, mg/cc	4.305	4.450	4.451	4.460	4.486	4.490	4.490
Final Cd Concentration, mg/cc	4.290	4.452	4.354	4.439	4.376	4.447	4.413
Total Weight of Residue, mgs/1	2.0	1.4	0.7	0.5	0.4	0.5	0.4
Material Balance for Cd, mgs							
Cd in Solution Initially	1214.9	1217.0	1222.4	1219.8	1229.5	1218.1	1240.1
Cd in Solution Final	1203.0	1207.7	1191.4	1210.4	1195.6	1198.8	1213.1
Cd Obtained from Flask Walls/2	6.8	5.5	5.2	5.9	6.3	5.9	7.8
Cd in Solution Precipitate	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1
Cd Deposited on Specimens	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-
Cd Unaccounted for	4.9	3.6	25.6	3.3	27.4	13.2	19.1
Specimens							
Material (1)	Zr 2-9	Zr 2-10	Zr 2-11	Zr 2-12	Zr 2-13	Zr 2-14	-
(2)	Zr 4-1	Zr 4-2	Zr 4-3	Zr 4-4	Zr 4-5	Zr 4-6	-
(3)	Zr, Nb-1	Zr, Nb-2	Zr, Nb-3	Zr, Nb-4	Zr, Nb-6	Zr, Nb-7	-
Change in Weight, $\mu g/cm^2$ (1)	-1.56	+1.80	+1.54	+3.24	+3.22	+2.52	-
(2)	+10.32	+0.39	+1.34	+1.58	+3.84	+2.02	-
(3)	-39.02	-1.16	+0.82	+2.06	+4.62	+1.52	-
Cd Deposited on Specimens, $\mu g/cm^2$ (1)	1.4	1.9	<0.2	<0.2	<0.2	1.2	-
(2)	<0.2	<0.2	<0.2	0.3	0.8	0.7	-
(3)	<0.2	0.3	<0.2	0.5	0.8	0.4	-

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

/2 Walls of flask washed with nitric acid after removing solution and rinsing flasks with water.

Table 10

Results of Bench Test #7

Flask #		1	2	3	4	5	6	7
Solution								
Initial pH		5.71	3.72	5.08	4.11	4.98	4.08	5.74
Final pH		6.73	6.70	5.82	5.80	4.92	4.29	6.17
Initial Resistivity, ohm-cm		268.	265.	22.5	22.5	22.4	22.2	262.
Final Resistivity, ohm-cm		273.	270.	23.3	23.7	23.7	23.7	277.
Initial Cd Conc, mg/cc		4.48	4.46	161.9	161.0	161.9	160.7	4.48
Final Cd Conc, mg/cc		4.43	4.36	181.0	185.2	177.9	187.1	3.72
Total Weight of Residue, mgs /1		32.9	20.8	141.6	98.9	4.5	2.5	1.2
Material Balance for Cd/mgs		Not accurately checked →						
Specimens								
Material	(1)	316 SST →				None	None	None
	(2)	Zirc-2 →						
	(3)	Zirc-4 →						
	(4)	High T Buna N →						
	(5)	Low T Buna N →						
	(6)	Silicon Rubber →						
Weight change, mg/cm^2	(1)	8.82	9.92	14.09	14.40			
	(2)	10.65	26.03	10.04	12.44			
	(3)	5.97	25.44	27.47	14.87			
	(4)	785.-824.	767.-840.	232.-263.	269.-327.			
	(5)	309.-938.	494.-717.	268.-373.	297.-464.			
	(6)	64.-292.	147.-196.	-102.- + 0.5	-49.- + 39.			
Cadmium Deposition, mg/dm^2	(1)	5.1	1.2	1.4	2.5			
	(2)	4.8	3.2	1.8	0.86			
	(3)	1.18	2.2	3.7-10.7	5.8-14.5			
	(4)	14.1	42.0	37.-68.	59.-189.			
	(5)	34.-37.	50.-63.	29.	87.-171.			
	(6)	8.	17.-30.	16.	11.-105.			
Force to break specimen, lbs.	(4)	72.5	81.0	72.2	66.8			
	(5)	26.8	20.8	49.2	44.8			
	(6)	14.0	21.5	25.8	24.4			
Ultimate length of 3" original spec, inches	(4)	12.00	12.09	11.11	11.02			
	(5)	9.13	9.74	18.79	16.43			
	(6)	3.38	7.05	11.11	9.96			
Ultimate length of 3" original spec, untested in $CdSO_4$, inches		High Temp. Buna-N		12.53-13.99				
		Low Temp. Buna-N		15.24-18.00				
		Silicon Rubber		9.11- 9.44				

/1 Residue is the weight of all solid material left on a filter after filtering the solution in the flasks after the test. It does not include cadmium adhering to the walls after rinsing.

Table 11

Results of Large Autoclave Test #1

Solution

emperature 400°F

Pressure 600 psig

Cadmium content, ppm Initial - 4500 ppm

After 100 hrs - 4155 ppm

After 500 hrs - 3905 ppm

pH Initial - 5.88

After 100 hrs - 6.20

After 500 hrs - 3.7

Residue of Filtered Solution After 500 Hours

Weight - 2.2969 grams

Analysis - Cadmium - 63.7%

Sulfate	13.0%
Iron	2.7%
Nickel	0.13%
Chromium	0.44%
Copper	0.06%

Material Balance for Cd, gms

Cd in Initial Solution	15.750
Cd in Final Solution	13.668
Cd in Residue	1.463

Coupons Subjected to 100 Hours at 400 F

Material	Spec	Wt Change mg/dm^2	Cd Deposition μg/cm^2	Total Metal Attack, Max, mg/dm^2	Total Metal Attack, Min, mg/dm^2	Hydrogen Generator Max, cc/dm^2
316 SST	13	-7.77	9.2	16.38	14.76	8.76
	15	-7.66	10.0	15.76	14.26	8.43
Zr-2	22	0.991	0.6	-	-	1.39
	24	0.656	0.3	-	-	0.92
Zr-4	14	0.975	0.7	-	-	1.36
	16	1.00	<0.2	-	-	1.40
Zr-Nb	9	1.34	5.1	-	-	1.88
	11	2.88	4.5	-	-	4.03
304 SST	1	-6.10	6.6	NA	NA	NA
	3	-4.37	5.9	NA	NA	NA

Table 11 (Continued)

Coupons Subjected to 400 Hours at 400°F

Material	Spec	Wt Change mg/dm²	Cd Deposition μg/cm²	Total Metal Attack, Max, mg/dm²	Total Metal Attack, Min, mg/dm²	Hydrogen Generator Max, cc/dm²
316 SST	17	-14.22	5.3	24.96	24.01	13.35
	18	-12.54	5.8	22.11	20.83	11.82
Zr-2	26	1.29	1.0	-	-	1.8
	27	0.914	1.9	-	-	1.28
Zr-4	18	2.32	1.1	-	-	3.25
	19	2.50	0.7	-	-	3.50
Zr-Nb	13	10.43	8.7	-	-	14.6
	14	10.21	7.3	-	-	14.3
304 SST	5	-10.22	4.7	NA	NA	NA
	6	- 9.94	4.6	NA	NA	NA

Coupons Subjected to 500 Hours at 400°F

Material	Spec	Wt Change mg/dm²	Cd Deposition μg/cm²	Total Metal Attack, Max, mg/dm²	Total Metal Attack, Min, mg/dm²	Hydrogen Generator Max, cc/dm²
316 SST	14	-13.84	6.6	26.10	24.38	13.95
	16	-11.70	6.7	22.42	20.45	11.99
Zr-2	23	1.75	0.7	-	-	2.45
	25	1.64	1.0	-	-	2.30
Zr-4	15	2.76	1.1	-	-	3.86
	17	2.51	1.3	-	-	3.52
Zr-Nb	10	10.08	8.0	-	-	14.1
	12	11.73	9.1	-	-	16.5
304 SST	2	-10.80	5.8	NA	NA	NA
	4	- 8.96	4.4	NA	NA	NA

Table 12

Results of Large Autoclave Test #2

Solution

Temperature	350°F		
Pressure	600 psig		
Cadmium content, ppm		Initial	- 4600 ppm
		After 100 hrs	- 4680 ppm
pH	Initial	- 5.90	
	After 100 hrs	- 4.35	

Residue of Filtered Solution After 100 Hours

Weight	- 0.5078 grams	
Analysis -	Cadmium	69.5%
	Sulfate	22%
	Iron	1.6%
	Nickel	0.09%
	Chromium	<0.04%
	Copper	0.02%

Material Balance for Cd, gms

Cd in Initial Solution	16.100
Cd in Final Solution	16.300
Cd in Residue	0.353

Coupons

None were included in this test.

Analysis for Impurities in Solution Filtrate After Test, ppm

Aluminum	5.65	Nickel	9.6
Calcium	0.65	Lead	0.1
Cobalt	0.09	Silicon	1.04
Chromium	0.06	Titanium	0.52
Copper	0.03	Zinc	0.56
Iron	13.9	Zirconium	0.09
Magnesium	0.15		
Manganese	1.09		
Niobium	0.11		

Table 13

Results of Large Autoclave Test #3

Solution

Temperature	350°F		
Pressure	600 psig		
Cadmium content ppm		Initial	4380
		After 100 hrs	4325
		After 500 hrs	4050
pH	Initial	3.4	
	After 100 hrs	3.7	
	After 500 hrs	3.45	

Residue of Filtered Solution After 500 Hours

Weight	0.3414 grams	
Analysis	Cadmium	84.2 %
	Sulfate	10 %
	Iron	0.02%
	Nickel	<0.03%
	Chromium	<0.04%
	Copper	0.01%

Material Balance for Cd, gms

Cd in Initial Solution	15.300
Cd in Final Solution	14.200
Cd in Residue	0.287

Coupons Subjected to 100 Hours at 350°F

Material	Spec	Wt Change mg/dm²	Cd Deposition μg/cm²	Total Metal Attack, Max, mg/dm²	Total Metal Attack, Min, mg/dm²	Hydrogen Generator Max, cc/dm²
316 SST	38	-5.76	2.00	10.93	9.81	5.84
	40	-7.22	2.17	13.09	11.83	7.00
Zr-2	49	0.230	<0.2	-	-	0.32
	55	0.083	0.51	-	-	0.12
Zr-4	45	0.451	<0.2	-	-	0.63
	47	-2.06	<0.2	-	-	-
Zr-Nb	40	2.39	1.82	-	-	3.34
	42	2.41	2.22	-	-	3.48
304 SST	27	-5.21	1.57	NA	NA	NA
	28	-6.54	1.85	NA	NA	NA

Table 13 (Continued)

Coupons Subjected to 400 Hours at 350°F

Material	Spec	Wt Change mg/dm²	Cd Deposition µg/cm²	Total Metal Attack, Max, mg/dm²	Total Metal Attack, Min, mg/dm²	Hydrogen Generator Max, cc/dm²
316 SST	41	-10.91	3.37	19.04	17.92	10.18
	43	- 8.87	3.42	16.81	15.89	8.99
Zr-2	51	0.594	<0.2	-	-	-
	53	0.443	0.2	-	-	-
Zr-4	42	0.814	<0.2	-	-	-
	46	1.91	0.41	-	-	-
Zr-Nb	35	5.01	2.99	-	-	-
	36	5.25	2.86	-	-	-
304 SST	32	-9.22	2.68	NA	NA	NA
	34	-7.25	2.99	NA	NA	NA

Coupons Subjected to 500 Hours at 350°F

Material	Spec	Wt Change mg/dm²	Cd Deposition µg/cm²	Total Metal Attack, Max, mg/dm²	Total Metal Attack, Min, mg/dm²	Hydrogen Generator Max, cc/dm²
316 SST	42	-11.19	3.39	19.36	18.21	10.35
	45	- 9.85	3.45	17.71	16.42	9.47
Zr-2	50	0.567	<0.2	-	-	0.79
	54	0.230	0.48	-	-	0.32
Zr-4	44	1.35	<0.2	-	-	1.89
	48	1.51	<0.2	-	-	2.12
Zr-Nb	37	6.54	2.91	-	-	9.15
	38	5.65	2.99	-	-	7.90
304.SST	30	-8.76	3.49	NA	NA	NA
	31	-7.76	3.35	NA	NA	NA

Analysis for Impurities in Solution Filtrate After Test, ppm

Aluminum	2.32	Manganese	2.32	Zirconium	0.08
Calcium	0.93	Niobium	0.08		
Cobalt	0.13	Nickel	11.2		
Chromium	0.14	Lead	0.15		
Copper	0.06	Silicon	1.08		
Iron	15.5	Titanium	0.50		
Magnesium	0.12	Zinc	0.31		

Table 14

Results of Autoclave Tests 4 through 9

Test Number	4	5	6	7	8	9
Temp, °F	350	350	300	250	300	300
Pressure, psig	600	600	600	600	600	600
Duration, hrs.	100	100	100	100	100	100
Cd Content, ppm						
Initial	4470	4470	4580	4580	4200	4200
Final	4325	4025	4540	4475	4135	4000
Solution pH						
Initial	5.34	4.05	5.46	5.44	5.35	5.39
Final	4.69	4.35	5.01	5.88	5.22	5.00
Weight of Residue, gms	1.529	1.991	0.333	0.120	0.172*	0.418**
Residue Analysis, %						
Cadmium	70.1	75.0	73.1	54.6	78.7	66.1
Sulfate	-	-	-	-	-	-
Iron	0.18	0.32	2.1	4.2	1.26	3.82
Nickel	0.041	0.013	0.08	0.15	0.048	0.053
Chromium	0.085	0.024	0.41	0.23	0.20	0.10
Copper	0.26	0.14	0.11	0.85	0.20	0.76

* Small amounts of additional crystalline matter adhering to specimens, clave and holder.

** Large amounts of additional crystalline matter adhering to specimens, clave and holder.

Table 14 (Continued)

Results of Large Autoclave Tests

Cd Material Balance, gms						
Cd in Initial Soln	28.434	20.951	31.529	22.850	28.90	21.714
Cd in Final Soln	27.501	18.998	31.527	22.327	28.283	19.960
Cd in Residue	1.071	1.493	0.234	0.067	0.135	0.276
Remarks	Cleaned Clave, Liq Full	Cleaned Clave, Liq Full	Cleaned Clave, Liq Full	Cleaned Clave, Liq Full	Semi-Passivated Clave, Liq Full	Passivated Clave, Liq Full
Analysis of Test Solution Filtrate after Test, ppm						
Aluminum	0.156	3.21	0.369	0.314	0.543	
Calcium	1.13	1.10	1.31	1.41	1.24	1.27
Cobalt	0.234	0.183	0.123	<0.08	<0.08	<0.08
Chromium	0.140	0.037	0.057	0.149	<0.08	<0.08
Copper	0.140	0.292	0.246	2.36	0.054	0.060
Iron	62.5	78.0	24.60	33.80	3.88	17.90
Magnesium	0.156	0.256	0.123	0.118	0.058	0.149
Manganese	1.56	1.10	1.025	0.864	1.16	2.24
Niobium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Nickel	15.60	14.60	6.56	0.369	1.32	2.46
Lead	0.273	0.401	0.205	0.495	0.093	0.276
Silicon	0.507	0.453	0.279	0.212	0.217	0.254
Titanium	<0.008	0.022	0.025	<0.008	0.027	0.022
Zinc	1.01	3.65	1.35	1.02	1.63	1.27
Zirconium	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08

In order to determine the effect of test conditions on the impurity level in the solutions after filtering to remove the residue, untested solutions were analyzed spectrographically. Typical results are shown in Table 15. Most of these elements were checked in the test filtrates, but not reported because the levels did not change. In the autoclave tests, the amount of material deposited on the coupons and on the autoclave walls was insignificant compared to the residue and was accordingly not accounted for.

Some of the residues were analyzed by X-ray diffraction methods in order to determine the compounds present. The "d" spacings and relative intensities of two typical residues are shown in Table 16. These patterns could not be matched to any reported by the National Bureau of Standards.

C. Loop Studies

One loop test was run at 350°F bulk fluid temperature for a period of 90 hours after many false starts. The heater, unto which slipped the cylindrical specimens, was fabricated with aluminum cladding. This was done to insure that these specimens would be held tightly at test conditions due to the differential coefficients of expansion of the various materials. The heater surface and the specimens inside diameters were machined such that there was a loose fit at room temperature, but an interference fit at 350°F.

In order to prevent severe corrosion attacks to the aluminum clad heater, its surface was first preconditioned by the Alumilite Harcoat treatment, which formed an oxide protective coating of up to 0.002 inch.

The heaters, which exited from the loop through a packing gland at the top of its housing, had to be anchored down at the bottom end to prevent its being forced out of the system by the force of the loop pressure. Holes were drilled at the bottom end of the heater so the heater could be pinned. During the machining operation, the cladding was penetrated, opening a direct path of loop fluid to the heater internal. Repairs of the penetrations were attempted, all of them unsuccessfully. The area could not be welded because of the foreign matter present in the penetrations. New bottom end caps were made for the heaters and the old ones cut off. Welding of the end caps proved unsuccessful even though the weld area seemed to have been cleaned thoroughly. One heater was finally repaired.

It was installed in the loop for checkout, and when it was removed, severe pitting was found in the area of the top packing gland. Graphite-asbestos packing had inadvertently been used and was the probable cause of pitting. Additional heaters were ordered but would not be delivered for about four weeks. It was decided to run the test anyway using the pitted heater. If it failed during test little would be lost; if successful, four weeks delay could be avoided. The loop was flushed thoroughly to remove the remains of the packing material, which was changed to Teflon.

Table 15

Typical Impurity Analysis of $CdSO_4$ Solution Prior to Testing

Element	ppm	Element	ppm
Ag	0.0024	Na	< 0.8
Al	0.032	Nb	< 0.024
Au	< 0.24	Ni	0.032
B	< 0.008	P	< 0.8
Ba	< 0.024	Pb	< 0.024
Be	< 0.0024	Sb	< 0.08
Bi	< 0.008	Si	0.176
Ca	1.52	Sn	< 0.024
Co	< 0.08	Sr	< 0.024
Cr	< 0.024	Th	< 0.8
Cu	0.024	Ti	< 0.024
Fe	0.064	Ta	< 0.24
In	< 0.8	V	< 0.08
Mg	0.018	W	< 0.24
Mn	0.052	Zn	< 0.8
Mo	< 0.024	Zr	< 0.024

Table 16

X-Ray Diffraction Patterns of Two Typical Residues

Residue 1 "d" Spacing	Residue 1 Relative Intensity*	Residue 2 "d" Spacing	Residue 2 Relative Intensity, %
10.18		3.767	10
5.155	strong	3.410	30
3.845	strong	3.207	30
3.400		3.087	100
3.200		2.948	20
3.075	very strong	2.901	50
2.935		2.570	25
2.890		2.466	20
2.594		2.389	20
2.467		2.307	20
2.382		2.149	20
2.3025		2.130	20
2.1610		2.065	30
2.1215		2.003	35
2.0660		1.963	10
2.0015		1.897	10
1.9210		1.878	10
1.8800		1.805	35
1.8255		1.699	20
1.800	strong	1.645	25
		1.603	20
		1.523	10

*remainder are equally weak.

Note: Copper radiation used
Wave length 1.5417 Angstroms

Figures 8 and 9 show the position of the specimens on the heater and in the coupon holder respectively. The specimens on the heater totalled 21-1/2 inches long while the heated zone was only 18 inches long. Therefore specimens were tested in the same environment, at the same velocity, in contact with the aluminum heater, both with and without heat flux across the solution-specimen interface. The heated region is shown in Figure 8.

The specimens in the variable velocity holder, shown in Figure 9, were subjected to fluid velocities varying from 5.0 feet per sec at the inlet to 31.6 feet per sec at the outlet. These coupons, all in the same test environment, were to be used to determine the effect of fluid velocity on corrosion and cadmium deposition on the various materials.

The materials tested in the heat flux region were 316 stainless steel, Zircaloy-2 and Zircaloy-4. They were in the form of right circular cylinders with nominal dimensions of 0.815 inch O.D., 0.750 inch I.D. and 0.5 inch long. The materials tested in the coupon holder were 304 and 316 stainless steel, Zircaloy-2 and 4, and Zircaloy-2.5% niobium alloy. They were rectangular in shape 0.5 inch wide, 2-1/8 inches long, and 0.030-0.050 inch thick. Approximately one-half of this area was exposed to the flowing test solution.

The results of the test are shown in Tables 17 through 20. Table 17, in addition to listing other test conditions shows the analyses for pH, resistivity, cadmium, oxygen and chloride versus time during the test. The test section heat flux is shown at its nominal value of 75,000 Btu/hr, ft^2. It had been reduced to 65,000 Btu/hr-ft^2 for a period of 17 hours. In addition there were four test section power trips during the test, each lasting no more than 10 minutes. The trips of heater power were caused by momentary low flow indications in the test section housing, resulting from a back pressure momentarily existing when the makeup pump stroked. This phenomenon is being investigated further.

The concentrated cadmium sulfate solution was originally added to the makeup tank along with a calculated amount of sulfuric acid to result in a solution pH of 4.0. Bleed and feed between the loop and makeup tank was then initiated to equilibrate the two. The first sample, taken 1-1/2 hours after $CdSO_4$ addition, indicated that the two were near equilibirum but with a low pH as well as a low cadmium concentration. More $CdSO_4$ concentrate was added to the makeup tank. Samples taken the next morning are shown as the 18 hour samples. There is no explanation for still high cadmium concentrations found in the next set of samples taken that afternoon.

A day and one-half went by before the next set of samples was taken because of a weekend. These samples along with those taken near the end of the test indicate a continually dropping cadmium concentration.

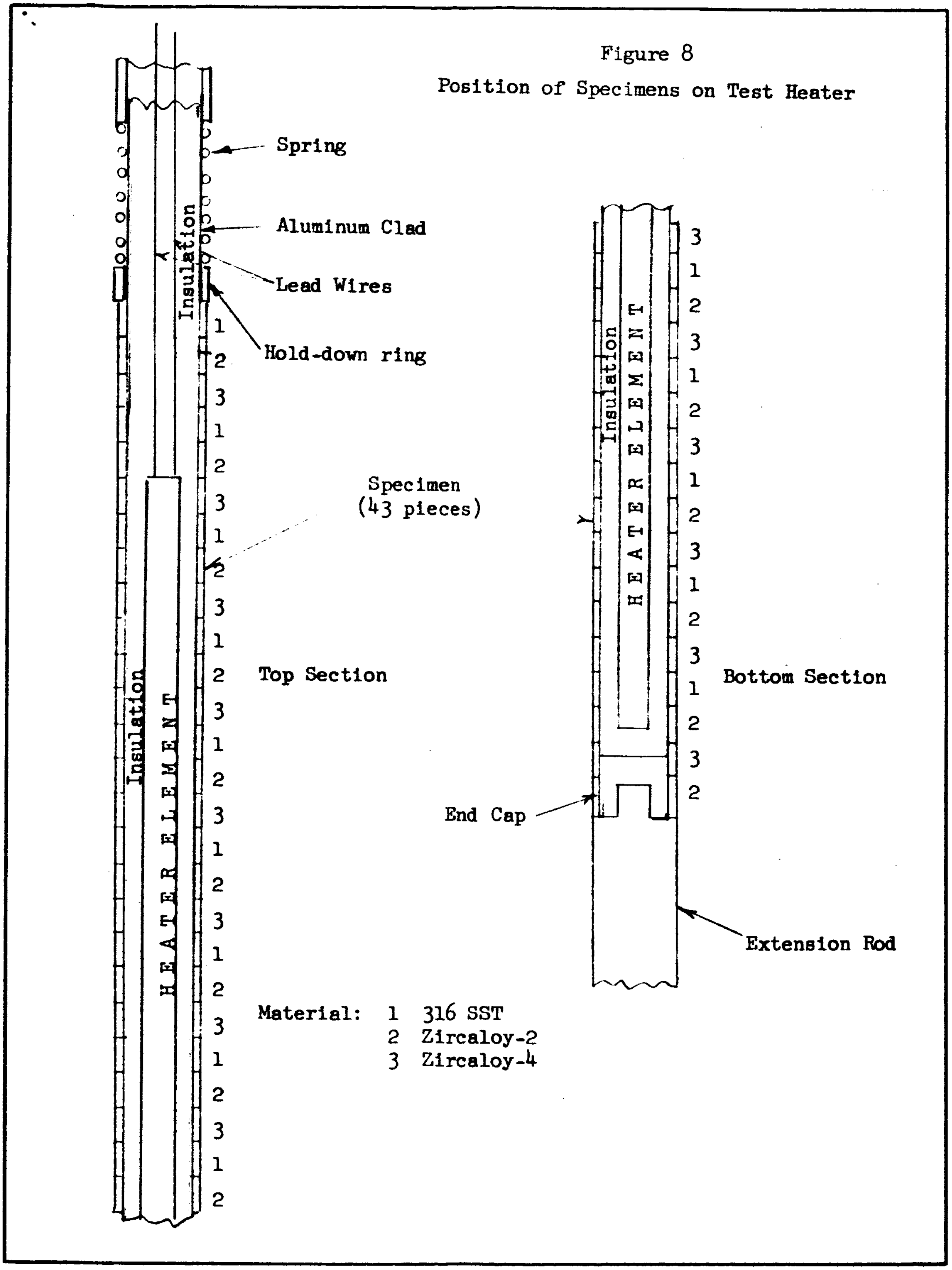
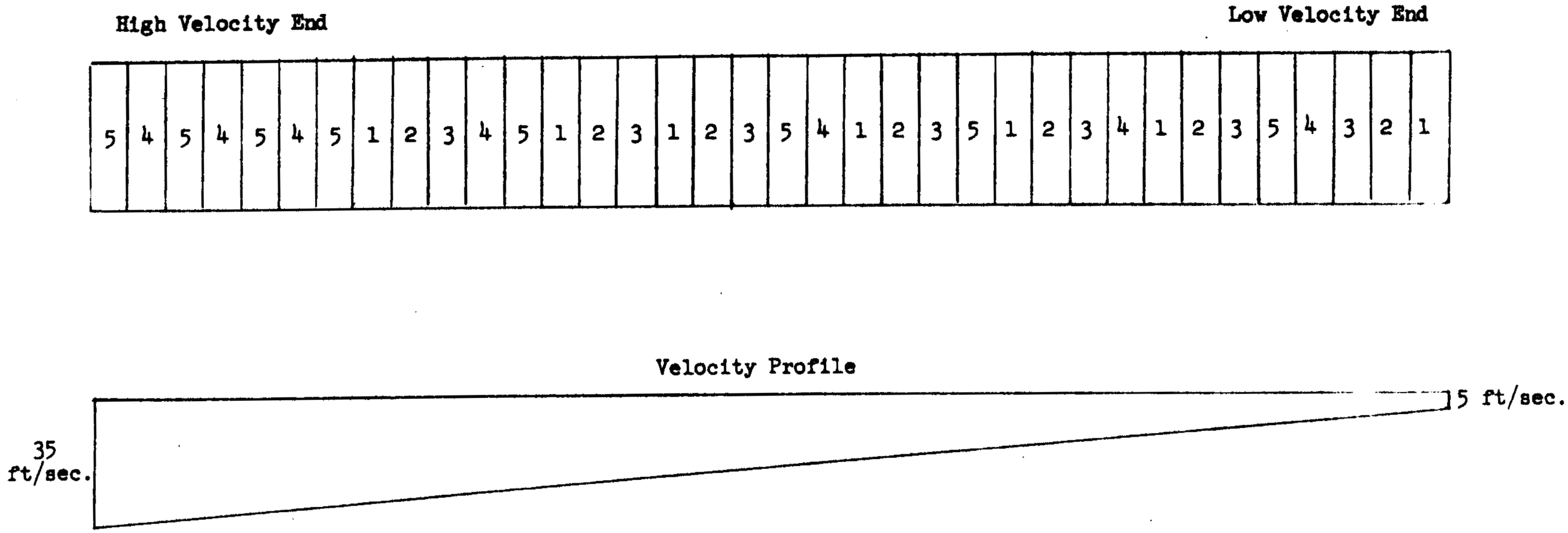


Figure 8

Position of Specimens on Test Heater

Figure 9

Position of Coupons in the Variable Velocity Holder



Materials:
1 Zircaloy-2
2 Zircaloy-4
3 Zirc-2.5% Nb
4 304 SST
5 316 SST

Table 17

Results of Loop Test - Solution Chemistry vs Time

Time After Turning on Power, Hrs.	Cadmium Conc., mg/cc	Solution pH	Solution Resistivity, ohm-cm	Oxygen Content, ppm	Chloride Content, ppm
1. 1-1/2 hrs before power	0	6.34	1.5×10^6	0.04	0.17
2. Zero, at Time Power Turned On	0	-	-	-	0.05
3. 2	Cadmium added to Makeup Tank (MuT) and bleed and feed begun.				
4. 3-1/2	Loop 4.040	2.85	260	-	0.08
	MuT 4.110	2.82	250	-	0.04
	(additional cadmium added to MuT)				
5. 18-1/2	Loop 3.925	2.78	245	<0.02	0.31
	MuT 4.475	2.83	240	-	0.02
6. 24	Loop 4.250	2.80	240	<0.02	0.30
	MuT 4.540	2.80	235	<0.02	0.08
7. 67	Loop 3.975	2.85	250	-	1.48
	MuT 4.050	2.85	258	-	1.00
8. 89-1/2	Loop 3.875	2.80	252	<0.02	1.40
	MuT 3.840	2.85	250	<0.02	2.12
9. 93-1/2	Power Off.				

Power trips occurred at 1, 4, 9 and 81 hours for no more than 10 minutes each time.

Table 18

Analyses of Loop Test Residues and Filtrates

Analyses of /1 Residues, %	1	2	3	4	5	6	7	8	9
Ag	0.11	0.04	0.04	0.14	<0.01	<0.01	<0.01	<0.01	0.002
Al	2.8	5.8	7.2	1.4	<0.03	0.78	20	<0.03	0.025
Ca	0.08	0.75	0.36	0.10	0.03	0.003	0.14	0.03	0.03
Cd	1.1	2.7	2.6	0.96	77.2	72.4	29.5	63.9	80.1
Cr	6.0	1.3	1.9	1.4	<0.1	<0.1	0.23	<0.1	0.07
Cu	0.95	0.20	0.31	0.18	<0.01	0.02	0.23	<0.01	0.005
Fe	26.	18.	36.	35.	0.25	0.18	0.37	0.18	0.25
Mg	0.30	0.80	0.10	3.0	0.03	<0.01	0.03	0.01	0.10
Mn	0.28	0.25	0.22	0.19	<0.01	<0.01	<0.01	<0.01	0.015
Mo	0.90	0.20	0.56	0.70	<0.03	<0.03	0.05	<0.03	0.007
Ni	1.6	0.32	1.5	0.59	<0.1	<0.1	0.17	<0.1	0.04
Pb	1.5	0.30	0.25	0.30	<0.1	<0.1	<0.1	<0.1	0.03
Si	2.2	11.	2.9	3.2	0.15	0.03	0.21	0.12	0.056
Sn	0.35	<0.1	0.16	<0.1	<0.1	<0.1	<0.1	<0.1	0.02
Th	3.0	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.01
Ti	0.21	0.58	0.45	0.43	<0.1	<0.1	0.30	<0.1	<0.001
Zr	0.14	0.07	0.01	0.05	<0.01	<0.01	0.42	0.11	<0.001
S	-	-	-	-	-	-	6.4	4.3	-
SO_4	-	-	-	-	-	-	0.50	2.29	-
Wt, mgs	1.41	2.12	418.9	486.5	15.	117.1	427.0	4,547.8	8,370

Analysis of Filtrates, ppm	10	11
Ag	<0.002	<0.002
Al	0.282	0.310
Ca	1.18	1.70
Cd ppm	3075-3175	4050-4170
mg/cc	3.075-3.175	4.050-4.170
Co	0.049	0.101
Cr	0.106	0.093
Cu	0.218	0.263
Fe	29.4	38.7
Mg	0.288	0.510
Mn	0.618	0.890
Mo	<0.02	0.031
Ni	10.6	15.5
Pb	0.589	0.850
Si	0.53	1.31
Ti	0.021	0.050
Zn	0.940	1.86
Zr	<0.05	<0.05

/1 These analyses were performed for the metallic elemental constituents, with the exceptions of sulphur and sulphate where applicable. It does not include oxygen or hydrogen which are probably the remainders.

Sample

1 - In-line filter at test completion
2 - Residue from filtering 1 gal. of loop fluid at test completion
3 - Deposit from bottom of makeup tank
4 - Residue from filtering loop drain and makeup tank composite
5 - Yellow deposit scraped from cylindrical specimens
6 - Deposit taken from between heater and specimens near bottom
7 - Deposit obtained from rinsing heater and specimens
8 - Deposit found in stagnant region just below test heater
9 - Deposit found in main loop heater pipe when loop was dismantled
10 - Filtrate from Sample 4
11 - Filtrate from Sample 2

Table 19

Results of Loop Test Weight Change and Cadmium Deposition on Specimens Mounted on Heater

Material	Position from Top of Heater	Spec. No.	Pre-test Wt, gms	Post-test Wt, gms	Max wt(1) Change mg/dm²	Min wt(1) Change gm/dm²	Cadmium Deposition µg/cm² Pos. A(2)	Pos. B
316 SST	1	2-46	5.203985	5.203612	-4.50	-2.25	0.37	0.42
	4	61	5.247324	5.246388	-11.46	-5.73	0.21	0.42
	7	48	5.257748	5.255665	-27.94	-13.97	0.27	2.06
	10	49	5.196138	5.193889	-27.16	-13.58	11.1	14.3
	13	50	5.236759	5.234418	-28.27	-14.14	13.8	8.65
	16	51	5.263855	5.262141	-21.35	-10.67	5.31	3.96
	19	52	5.239686	5.237496	-28.27	-14.14	4.80	5.31
	22	53	5.171105	5.168602	-30.23	-15.12	1.32	2.23
	25	54	5.206415	5.204290	-25.66	-12.83	2.57	2.83
	28	55	5.252100	5.248896	-38.70	-19.35	0.57	0.73
	31	56	5.220417	5.218128	-28.02	-14.01	0.63	0.33
	34	57	5.236961	5.238428	-25.64	-12.82	0.32	0.30
	37	58	5.150039	5.149669	- 4.53	- 2.27	0.59	1.13
	40	47	5.157103	5.156401	- 8.59	- 2.30	0.47	0.40
Zirc-4	3	6-50	4.191278	4.191780	+ 6.09	+ 3.04	0.26	0.19
	6	51	4.227009	4.227585	+ 7.05	+ 3.53	0.54	0.53
	9	52	4.209269	4.211634	+28.95	+14.47	35.7	0.65
	12	53	4.168075	4.170773	+32.66	+16.33	4.07	2.73
	15	54	4.235895	4.238585	+32.57	+16.28	4.66	11.6
	18	55	4.186552	4.188201	+20.55	+10.28	1.59	1.98
	21	56	4.210323	4.211868	+18.73	+ 9.36	1.93	0.68
	24	57	4.177465	4.178883	+17.17	+ 8.58	1.39	0.76
	27	58	4.224266	4.176897	-579.79	-289.90	0.48	0.19
	30	59	4.256033	4.256963	+11.28	+ 5.64	<0.1	0.17
	33	60	4.248635	4.250703	+25.31	+12.66	1.23	0.42
	36	61	4.228226	4.229363	+13.92	+ 6.96	0.37	0.63
	39	62	4.241344	4.243295	+23.88	+11.94	0.55	1.15
	42	63	4.202225	4.203988	+21.58	+10.79	0.48	0.92
Zirc-2	2	3-56	4.149962	4.150373	+ 5.03	+ 2.52	0.30	<0.1
	5	57	4.237181	4.237682	+ 6.04	+ 3.02	<0.1	<0.1
	8	58	4.208392	4.210231	+12.55	+ 6.27	0.24	4.34
	11	59	4.178503	4.180605	+25.36	+12.68	3.83	1.93
	14	60	4.171520	4.174656	+38.38	+19.19	9.90	0.86
	17	61	4.107904	4.109355	+17.76	+ 8.88	0.89	<0.1
	20	62	4.148382	4.150507	+25.76	+12.88	0.83	1.14
	23	63	4.184899	4.186351	+17.77	+ 8.89	2.49	<0.1
	26	64	4.175834	4.225131	+595.37	+297.69	0.47	<0.1
	29	65	4.193146	4.193858	+ 8.60	+ 4.30	<0.1	<0.1
	32	66	4.200020	4.201340	+15.94	+ 7.97	<0.1	<0.1
	35	67	4.181515	4.183396	+22.72	+11.86	<0.1	<0.1
	38	68	4.201782	4.204512	+32.97	+16.49	1.06	<0.1
	41	69	4.166615	4.168206	+19.22	+ 9.61	<0.1	0.50
	43	70	4.151573	4.152408	+10.22	+ 5.11	<0.1	<0.1

(1) Area used to determine max wt change was 0.083 dm², and 0.166 dm² used to determine min wt change

(2) Position A&B are 180° apart on outside surface

Table 20

Results of Loop Test

Weight Change and Cadmium Deposition on
Flat Specimens in Variable Velocity Holder

Material	Position from Low Velocity End	Specimen Number	Flow Velocity Ft/sec	Pretest Wt. gms	Total Area dm^2	Exposed Area dm^2	Post-test Wt. gms	Min. Wt. Change/1 mg/dm^2	Max. Wt. Change/2 mg/dm	Cadmium Deposition Top $\mu g/cm^2$	Cadmium Deposition Bottom $\mu g/cm^2$
316 SST	5	2-26	5.5	4.256459	0.138	0.0640	4.255842	-4.471	-9.641	4.3	4.9
	13	25	7.0	4.338833	0.140	0.0645	4.338214	-4.421	-9.597	3.9	4.0
	18	24	8.4	4.256594	0.138	0.0640	4.256045	-3.978	-8.578	4.1	3.9
	25	23	11.8	4.332760	0.139	0.0640	4.332307	-3.259	-7.078	3.6	2.7
	30	22	16.8	4.327418	0.139	0.0640	4.326850	-4.086	-8.875	4.6	4.6
	32	21	19.6	4.254820	0.139	0.0645	4.254306	-3.698	-7.969	4.5	4.7
	34	20	24.2	4.331185	0.139	0.0640	4.330736	-3.230	-7.016	3.7	4.5
	36	19	31.6	4.324876	0.139	0.0640	4.324865	-0.079	-0.172	3.3	2.4
304 SST	4	8-13	5.3	4.052227	0.139	0.0645	4.051644	-4.194	-9.039	6.9	6.4
	9	12	6.1	4.121978	0.141	0.0645	4.121607	-2.631	-5.752	6.7	6.4
	17	11	8.1	4.074205	0.138	0.0640	4.073723	-3.427	-7.391	4.7	6.9
	26	10	12.5	4.079558	0.138	0.0640	4.079142	-3.014	-6.500	4.9	4.6
	31	9	17.9	4.121911	0.140	0.0640	4.121430	-3.436	-7.516	6.0	5.8
	33	8	21.6	4.122530	0.140	0.0645	4.122037	-3.521	-7.643	5.7	4.3
	35	7	27.4	4.125681	0.139	0.0640	4.125320	-2.597	-5.641	4.8	3.7
Zirc-4	2	6-27	5.1	3.970799	0.140	0.0645	3.971116	+2.264	+4.915	0.8	<0.1
	7	26	5.8	4.002762	0.139	0.0640	4.003197	+3.129	+6.797	0.9	<0.1
	11	25	6.5	3.979981	0.140	0.0645	3.980552	+4.079	+8.853	1.2	1.0
	15	23	7.5	4.006199	0.139	0.0640	4.006744	+3.921	+8.516	2.1	0.4
	20	22	9.1	3.933180	0.138	0.0640	3.933752	+4.145	+8.937	2.9	1.4
	23	21	10.5	4.016010	0.140	0.0645	4.016711	+5.007	+10.868	2.9	1.4
	28	20	14.2	4.000781	0.139	0.0640	4.001347	+4.072	+8.844	1.6	0.9
Zirc-2	1	3-34	5.0	4.673290	0.139	0.0640	4.673600	+2.230	+4.844	<0.1	<0.1
	8	33	6.0	4.661298	0.139	0.0640	4.661614	+2.273	+4.937	0.2	0.8
	12	32	6.7	4.658181	0.139	0.0640	4.658261	+0.515	+1.250	<0.1	<0.1
	16	31	7.8	4.670595	0.140	0.0640	4.670962	+2.621	+5.734	0.7	0.3
	21	30	9.6	4.783968	0.143	0.0655	4.784361	+2.748	+6.000	<0.1	0.2
	24	29	11.1	4.686942	0.139	0.0645	4.687418	+3.424	+7.380	0.7	0.3
	29	28	15.2	4.679738	0.140	0.0640	4.680106	+2.629	+5.750	0.3	<0.1
Zirc-Niob.	3	7-22	5.2	4.200806	0.140	0.0640	4.201320	+3.671	+8.031	0.4	1.9
	6	20	5.6	4.237783	0.141	0.0645	4.238536	+5.340	+11.674	<0.1	3.4
	10	19	6.3	4.227152	0.141	0.0645	4.228197	+7.411	+16.201	4.9	1.9
	14	18	7.2	4.236318	0.140	0.0640	4.237213	+6.393	+13.984	6.6	0.6
	19	17	8.8	4.211211	0.140	0.0645	4.211867	+4.686	+10.171	1.8	2.3
	22	16	10.0	4.173721	0.140	0.0640	4.174751	+7.357	+16.094	2.9	2.6
	27	15	13.3	4.216535	0.140	0.0640	4.217174	+4.564	+9.984	<0.1	0.9

/1 The minimum specimen wt. change per unit area is calculated using the total specimen area.

/2 The maximum specimen wt. change per unit area is calculated using the specimen area intentionally exposed to solution. The difference between this area and the total is the area underneath the Teflon strip used to position the specimens. Stagnant solution was in contact with this area under the strip.

The test was terminated after 90 hours because it was determined that a heater failure at this point, with subsequent release of insulation to the loop fluid, could mask the results of the specimens. It should be remembered that the heater being used was pitted to a depth of 0.010 inch out of a 0.030 inch thick aluminum cladding, in spots, prior to conducting this test. The deepest pits after test, and there were many of them, were 0.017 inch deep.

The weights and analyses of residues and analyses of filtrates of the solutions collected from the loop and makeup tank were shown in Table 18. At the end of the test, the loop fluid was partially filtered through a high pressure filter holder in the purification leg of the loop. A one gallon sample from the loop was then removed for analysis; the remainder of the loop being dumped to a 55 gallon drum into which the makeup tank contents were also dumped.

Tables 19 and 20 show the results of measurements taken from the specimens on the heater and those in the coupon holder. With the change of weight information available and the results of stripping specimens from autoclave tests, it was decided not to strip any of these specimens. The results of the solution stability, which will be discussed later, also indicated that additional effort was needed on further autoclave tests, not on gaining more information from these loop specimens.

Figure 10 is an overall view of the cylindrical specimens mounted on the heater, after test. The two areas marked are shown as closeups in Figures 11 and 12. At the end of the test, the yellowish residue was found adhering to the specimens. This residue was loosely adherent and was gently brushed off, collected and analyzed. It was found to contain about 75% cadmium. The ring at the top of the specimens is the hold down ring above which is mounted a spring during operation to prevent chattering of the specimens. The end cap, and the area where the cladding penetrations were made is below the specimens.

Figure 13 is a view of the coupons mounted in half of a variable velocity coupon holder. The outline of the flow area is clearly visible. It is also obvious that a certain amount of corrosion also occurred between the specimens and the Teflon tape used to prevent electrically connecting the coupons to the housing. This tape is squeezed together to seal, when the second half of the holder is positioned. However, liquid must have gotten between the tape and coupons.

Residues were found after the test in various places in the loop. A light yellow residue was found in the stagnant area at the bottom of the heated test section. A bright yellow residue was found adhering to the surface of some specimens and between the specimens and the heater. The residue collected from the bottom of the makeup tank and the precipitate from filtration of the loop and makeup tank fluid was a red color. The material balance for the test, shown in Table 21, indicates that much cadmium remained

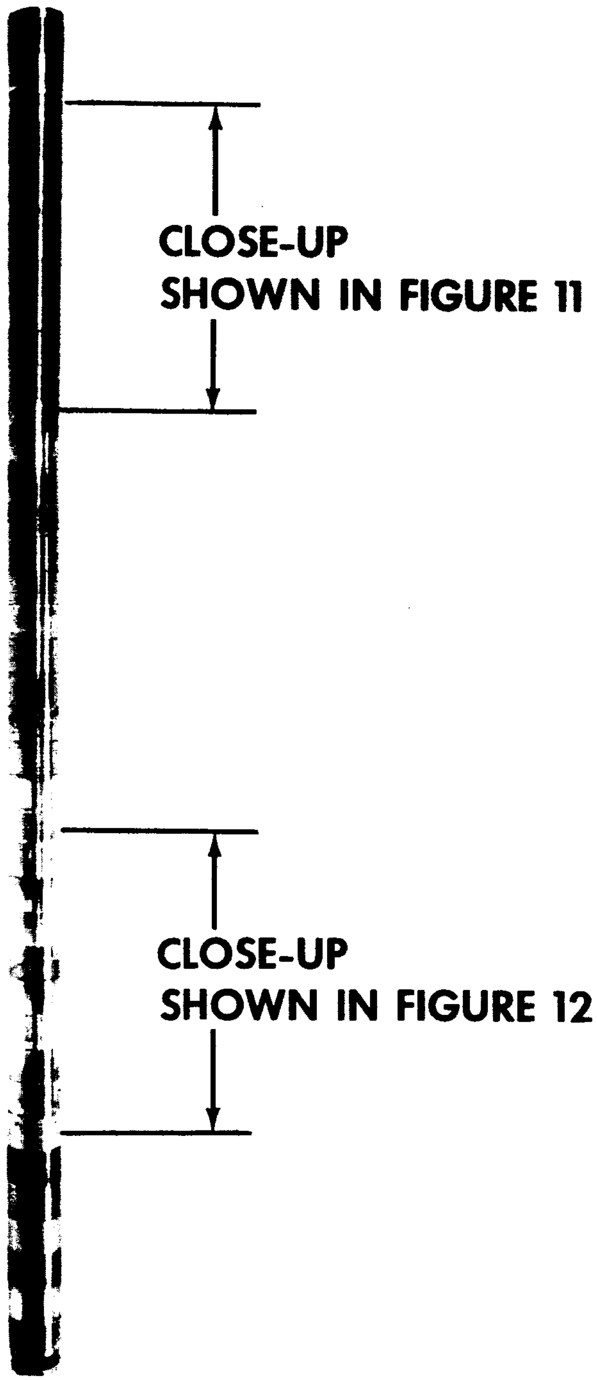


Figure 10 Loop Specimens Mounted on Heater After Test

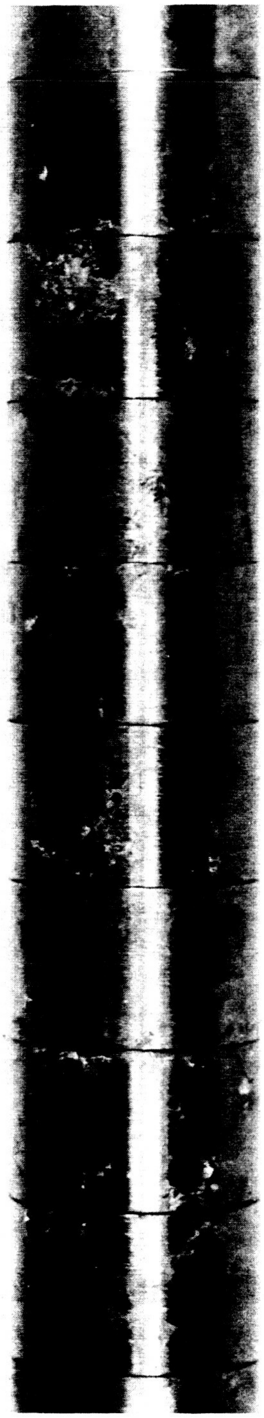


Figure 11

Closeup of Specimens Near Top of Heater - After Test

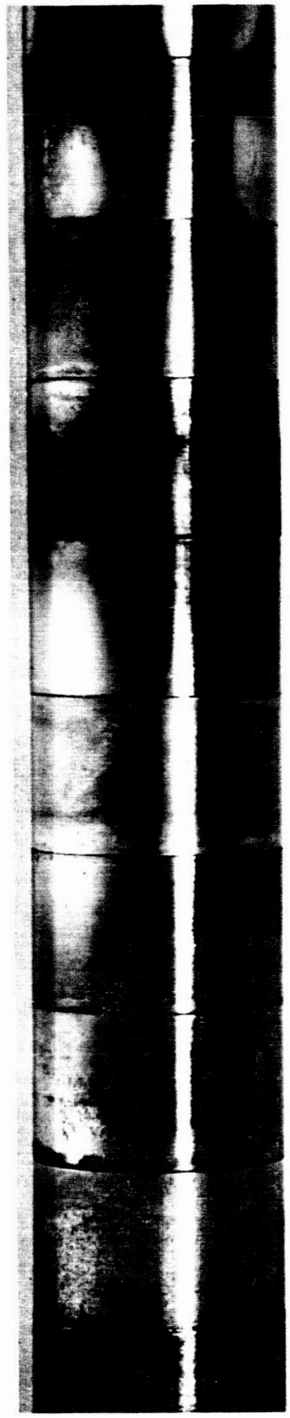


Figure 12

Closeup of Specimens Near Bottom of Heater - After Test

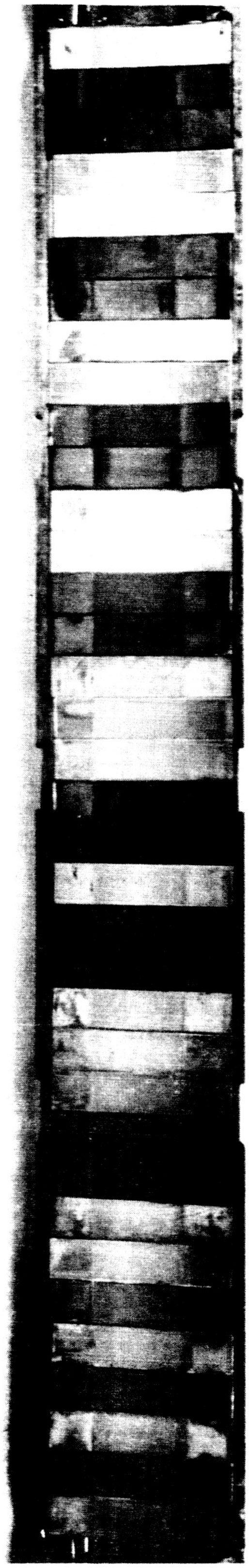


Figure 13

Coupons Mounted in Half of a Variable Velocity Holder

Table 21

Material Balance for Cadmium in Loop Test

Loop Volume = 18 liters

Makeup tank volume = 152 liters

Time After Turning On Power, Hrs.	Loop Cd. Conc., mg/cc	MUT Cd. Conc. mg/cc	Wt of Cd in Loop, gms	Wt of Cd in MUT, gms	Total Cadmium gms
3-1/2	4.04	4.11	72.6	62.5	697.6
18-1/2	3.925	4.475	70.6	680	750.6
24	4.25	4.540	7.65	690	766.5
67	3.975	4.050	71.5	616	687.5
89-1/2	3.875	3.840	69.6	584	653.6

Cadmium Additions: 745 gms at 2 hrs.
65.8 gms at 5 hrs.
810.8 gms Total

Cadmium Analysis After Test:

Composite of Loop and MUT Fluid (3.075 mg/cc)	650 gms
Total in All Residues	10 gms
	660 gms

Cadmium unaccounted for:

$$\frac{810.8 - 660}{810.8} \times 100 = 18.6\%$$

unaccounted for. Some of this has recently been found while preparing this loop for another program. The main loop heater was removed and a coral colored deposit found laying in the bottom of the horizontal pipe. The pieces of residue had a radius of curvature that was similar to the I.D. of the 3" pipe. No residue was adhering to either the heater or the pipe.

The loop was to be conditioned using a KOH solution at pH-10 for this next program. The loop was flushed and filled with demineralized water which was pumped around at 400°F with little decrease in resistivity. When the KOH was added, a pH of 10 could not be maintained (it dropped to 5.8) and large amounts of sulfate was found dissolved in the fluid. This was evidenced by a precipitate formed upon adding some barium chloride to a test tube of loop fluid. This indicates that an insoluble sulfate salt is present in the loop as a result of the cadmium sulfate test, and this residue is soluble in pH-10 solution.

The Alumilite Hardcoat surface applied to the test heater was severely attacked during the test. Many areas of the heater were completely free of this coating after the test, with bare aluminum metal visible.

VII. ANALYSIS OF RESULTS

A. Bench Tests

The bench or beaker tests were run to gain information about the use of cadmium sulfate solution in the CPLS, quickly and inexpensively. Originally, it was intended to operate only one or two tests, but the program was later expanded when the value of the tests was realized.

One or more of the flasks from each of the tests had only cadmium sulfate solution. These were the thermal stability tests, where the effect of solution pH on solution stability at atmospheric boiling conditions was studied. Figure 14 is a plot of the solution post-test pH versus the pretest pH. The dashed line represents the unchanged pH. A reduction in pH could indicate a preferential loss of cadmium from solution while an increase of pH could indicate a preferential loss of sulfate ion. This is not meant to suggest that both ions could not leave solution, but merely to suggest possible combinations of the two, thereby establishing a formula for the resulting residue. It should also be noted that it requires relatively little change of the hydrogen ion concentration in solution at the higher pH's (pH 5 to 7) to result in large pH changes when compared to the low pH range.

The loss of cadmium from solution was determined by two methods. The first involved measuring the cadmium content of the solution, by flame analysis, before and after the tests. The second method was to measure the amount of cadmium found out of solution at various locations in the test apparatus and use the sum as an indication of the amount of cadmium lost from solution. The second method is more accurate than the first and was considered the most reliable measurement of the degree of instability of the cadmium sulfate solution. The accuracy of the various analytical methods will be discussed later.

The percentage loss of cadmium from solution is shown in Figure 15 as a function of pretest solution pH. The cadmium loss shown is the sum of all cadmium found out of solution relative to the initial weight of cadmium in the solution. The sources of this cadmium are: (1) residue on the flask walls, and (2) precipitate filtered from the solution. These results are also tabulated in Tables 22 and 23. Most of this cadmium was deposited on the walls of the flasks. The variation of pretest solution pH from about 2 to 7 had little effect on the amount of cadmium lost from solution which generally appears to be .2 to .6%. At a solution pH of 6, the solution in two flasks, from two different tests, experienced cadmium losses of about 1.2%. There is no explainable reason for these losses. The deviation from other test results cannot be accounted for by known experimental errors.

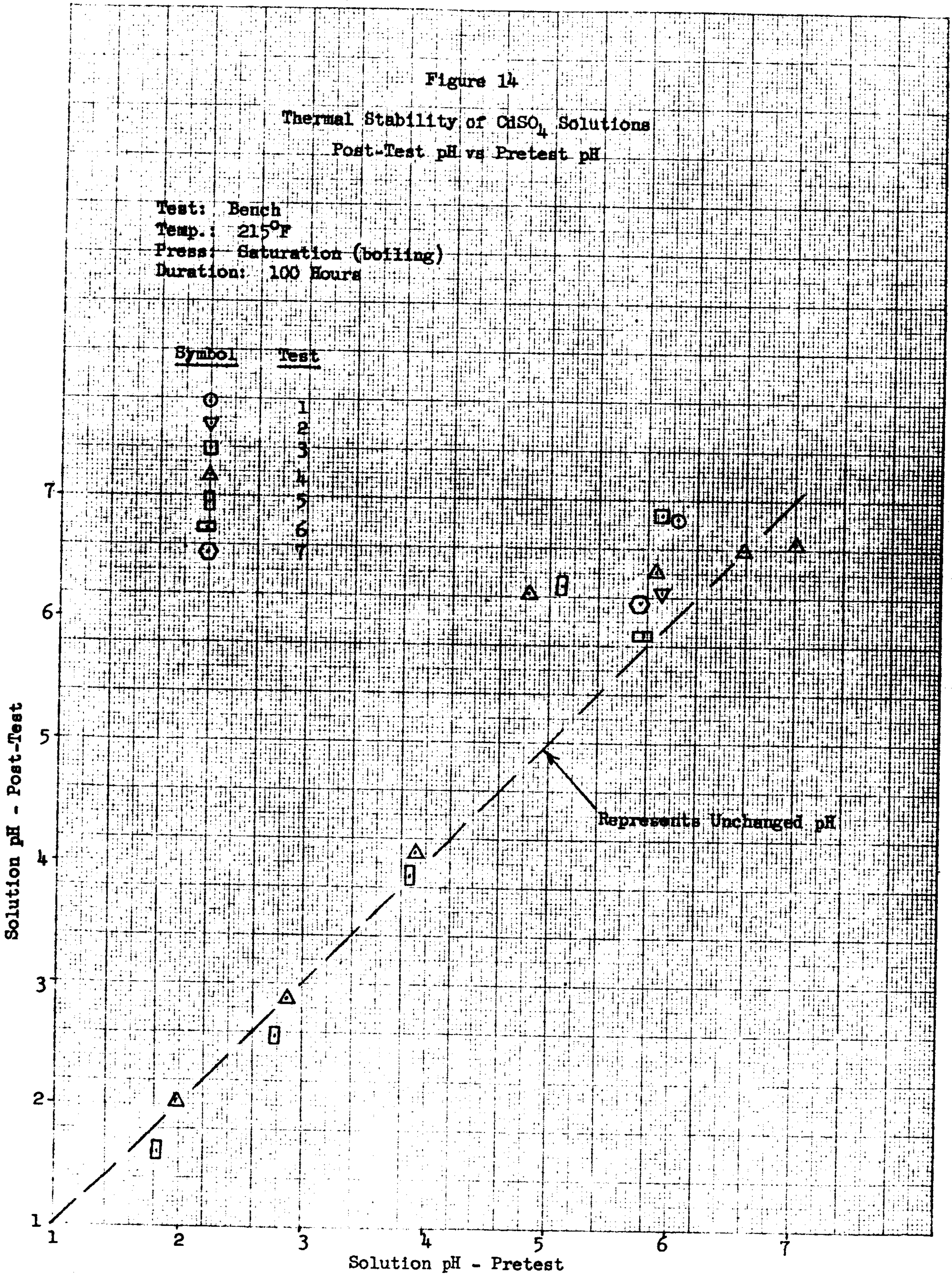


Figure 14
Thermal Stability of $CdSO_4$ Solutions
Post-Test pH vs Pretest pH
Test: Bench
Temp.: 215°F
Press: Saturation (boiling)
Duration: 100 Hours
Symbol
Test
1
2
3
4
5
6
7
Represents Unchanged pH
Solution pH - Post-Test
Solution pH - Pretest
1
2
3
4
5
6
7

Figure 15

Thermal Stability of $CdSO_4$ Solutions - Bench Tests

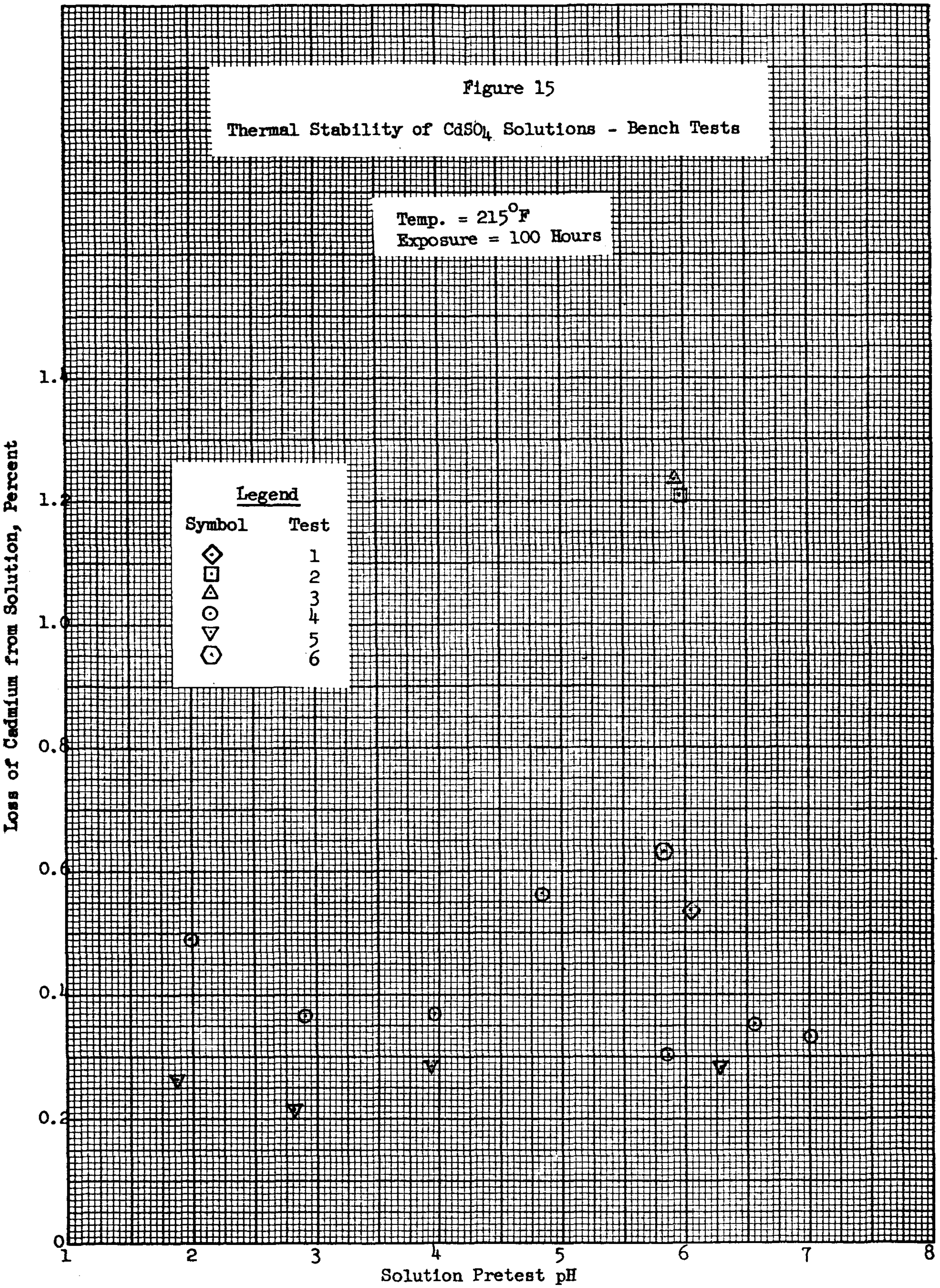


Table 22

Cadmium Found in Residues and Deposits, Percent

$(\frac{Cd \times 100}{Cd\ Init})$

Flask	BT#	1	2	3	4	5	6	7
1	precip - p	.011	<.01	36.12	.010	<.01	<.01	1.85
	spec - s	.01	.01	.03	N	<.01	<.01	3.51
	walls - w	.305	.840	3.82	.473	.254	.560	NA
	Total - T	.33	.85	39.97	.48	.25	.56	NA
2	p	.010	.020	32.89	.010	<.01	<.01	0.665
	s	<.01	<.01	.11	N	<.01	<.01	7.24
	w	.388	.825	2.47	.348	.266	.452	NA
	T	.40	.85	35.47	.36	.27	.45	NA
3	p	<.01	.010	27.65	<.01	<.01	<.01	0.156
	s	<.01	<.01	.03	N	N	<.01	0.125
	w	.349	.921	3.62	.364	.276	.425	NA
	T	.35	.93	31.30	.36	.28	.43	NA
4	p	<.01	.020	2.20	.010	<.01	<.01	0.102
	s	<.01	.02	.12	N	N	<.01	0.361
	w	.180	.945	1.69	.553	.282	.484	NA
	T	.18	.99	4.01	.56	.28	.48	NA
5	p	.211	.060	2.30	.010	<.01	<.01	<.01
	s	<.01	.01	.21	N	<.01	<.01	N
	w	.633	1.64	3.40	.293	.271	.512	NA
	T	.84	1.71	5.91	.30	.27	.51	NA
6	p	.021	.030	.201	<.01	<.01	<.01	<.01
	s	.03	.01	.18	N	N	<.01	N
	w	.971	1.18	2.50	.350	.260	.484	NA
	T	1.02	1.22	2.88	.35	.26	.48	NA
7	p	.075	.020	.086	.010	.01	.01	.021
	s	N	N	N	N	N	N	N
	w	.458	1.18	1.14	.317	.214	.629	NA
	T	.53	1.20	1.23	.33	.21	.63	NA

Notes:

1. N - None
2. NA- Not Available

Table 23

Cd Found in Residue and Deposits,

$$\frac{Cd}{Cd\ init} \times 100$$

(No Specimens in Flasks)

Test	Flask	Precip.	Walls	Total	Initial pH	Final pH
1	7	.075	.458	.53	6.02	6.84
2	7	.020	1.18	1.20	5.94	6.20
3	7	.086	1.14	1.23	5.90	6.89
4	1	.010	.473	.48	1.98	2.02
	2	.010	.348	.36	2.88	2.88
	3	<.01	.364	.36	3.94	4.08
	4	.010	.553	.56	4.83	6.25
	5	.010	.293	.30	5.86	6.41
	6	<.01	.350	.35	6.56	6.60
	7	.010	.317	.33	7.01	6.68
5	3	<.01	.276	.28	3.91	5.10
	4	<.01	.282	.28	3.85	6.28
	6	<.01	.260	.26	1.86	1.59
	7	<.01	.214	.21	2.80	2.57
6	7	<.01	.629	.63	5.79	5.88
7	5*	<.01	NA**	NA	4.98	4.92
	6*	<.01	NA	NA	4.08	4.29
	7	.021	NA	NA	5.74	6.17

* 300 mg Cd/cc, all others 8.3 mg Cd/cc

** NA - Not Available

Some of the bench test flasks had metallic coupons suspended in solution to check the compatibility of solution and structural material. Figure 16 is a plot of post-test solution pH versus pretest pH for these tests. Each point represents one test flask with the results of any series of tests connected by straight lines. The post-test pH of the solutions from the aluminum tests all ended up at about pH-4, regardless of the pre-test pH.

The loss of cadmium from solution containing metal specimens is shown in Figure 17 as a function of pretest solution pH. The cadmium loss from solution for bench test 4 (no metallic specimens) is shown as a basis for comparing the effect of the presence of metallic specimens. The cadmium loss represents the sum of all cadmium found out of solution. This includes: (1) residue on flask walls, (2) precipitate filtered from solution, and (3) cadmium deposited on metallic surfaces. Again most of the cadmium was found on the flask walls. The results obtained from bench test 2 were not plotted because the source of the Zircaloy samples was uncertain. The data plotted in Figure 17 indicate:

1. The presence of aluminum contributes greatly to the loss of cadmium from solution. The loss of cadmium with aluminum specimens is as much as 100 times greater than that loss experienced with no aluminum.

2. In the presence of aluminum, the cadmium loss is less at pH from 5 to 7 than at pH less than 5.

3. At a pH greater than 5, the presence of stainless steel causes some increase in the solution instability (loss of cadmium). However, at pH 5 or less the presence of stainless steel has little effect on solution stability.

4. The presence of Zircaloy and inconel have little effect on solution stability.

The cadmium deposited on the surface of the metallic specimens is shown in Figure 18 as a function of solution pretest pH for the stainless steel, Zircaloy and inconel specimens. The deposition on the aluminum is generally many times greater than the depositions on the other specimens tested and is not known. With the exception of the type 347 stainless steel specimens, the cadmium deposition on the metal surfaces is unaffected by solution pretest pH. The 347 stainless steel exhibited a large increase in cadmium deposition above a pH of 6.

The weight of the metallic specimens was measured before and after the tests and the results for the Zircaloy, inconel and stainless steel are shown in Figure 19 as a function of solution pretest pH. For Zircaloy, the increase in specimen weight is a measure of the amount of hydrogen generated as a result of corrosion of the metallic specimens. The relationship between weight gain and corrosion for stainless steel and

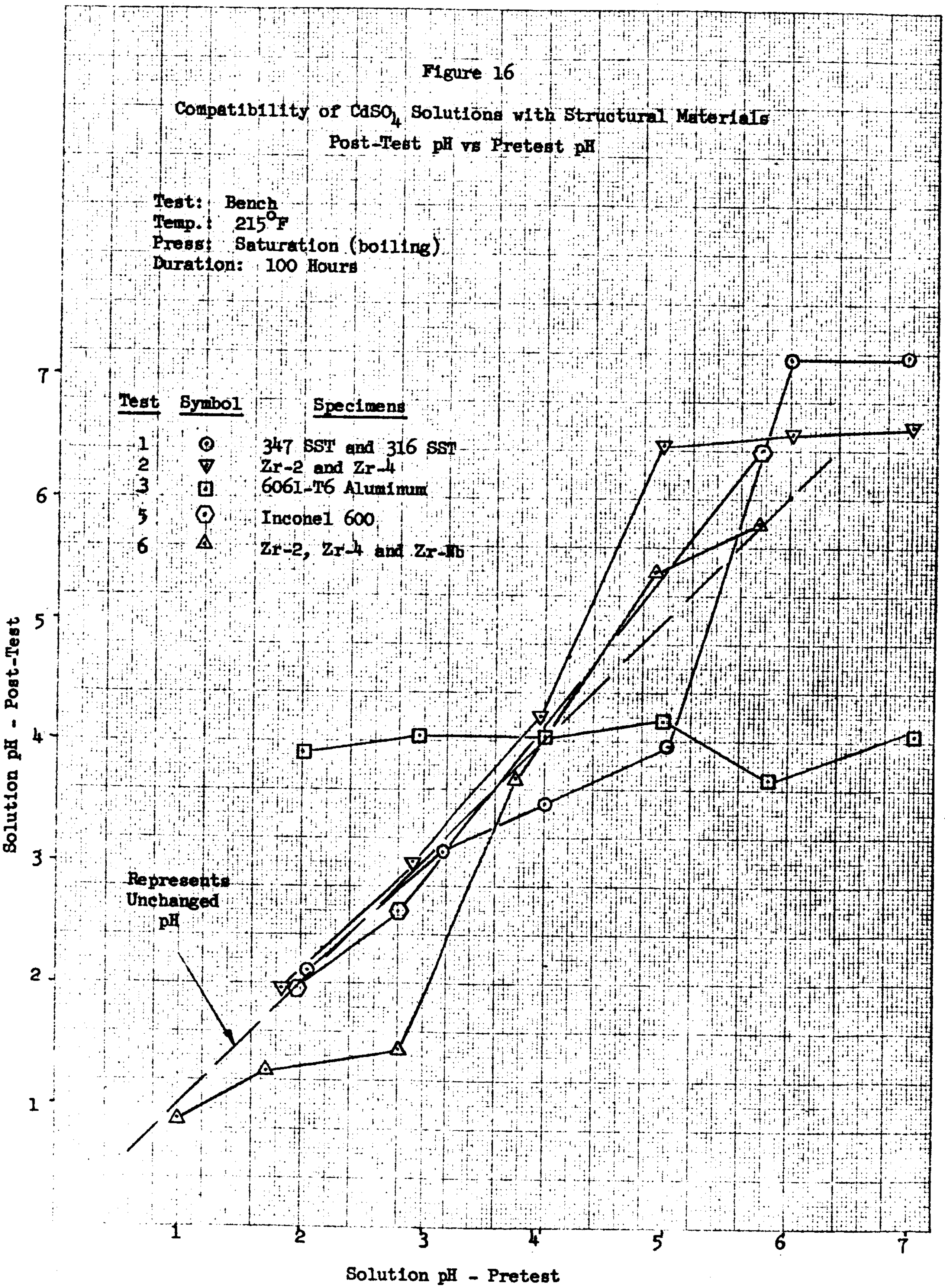


Figure 16
Compatibility of $CdSO_4$ Solutions with Structural Materials
Post-Test pH vs Pretest pH
Test: Bench
Temp.: 215°F
Press: Saturation (boiling)
Duration: 100 Hours
Test Symbol Specimens
1 347 SST and 316 SST
2 Zr-2 and Zr-4
3 6061-T6 Aluminum
5 Inconel 600
6 Zr-2, Zr-4 and Zr-Nb
Represents Unchanged pH
Solution pH - Post-Test
Solution pH - Pretest
1
2
3
4
5
6
7

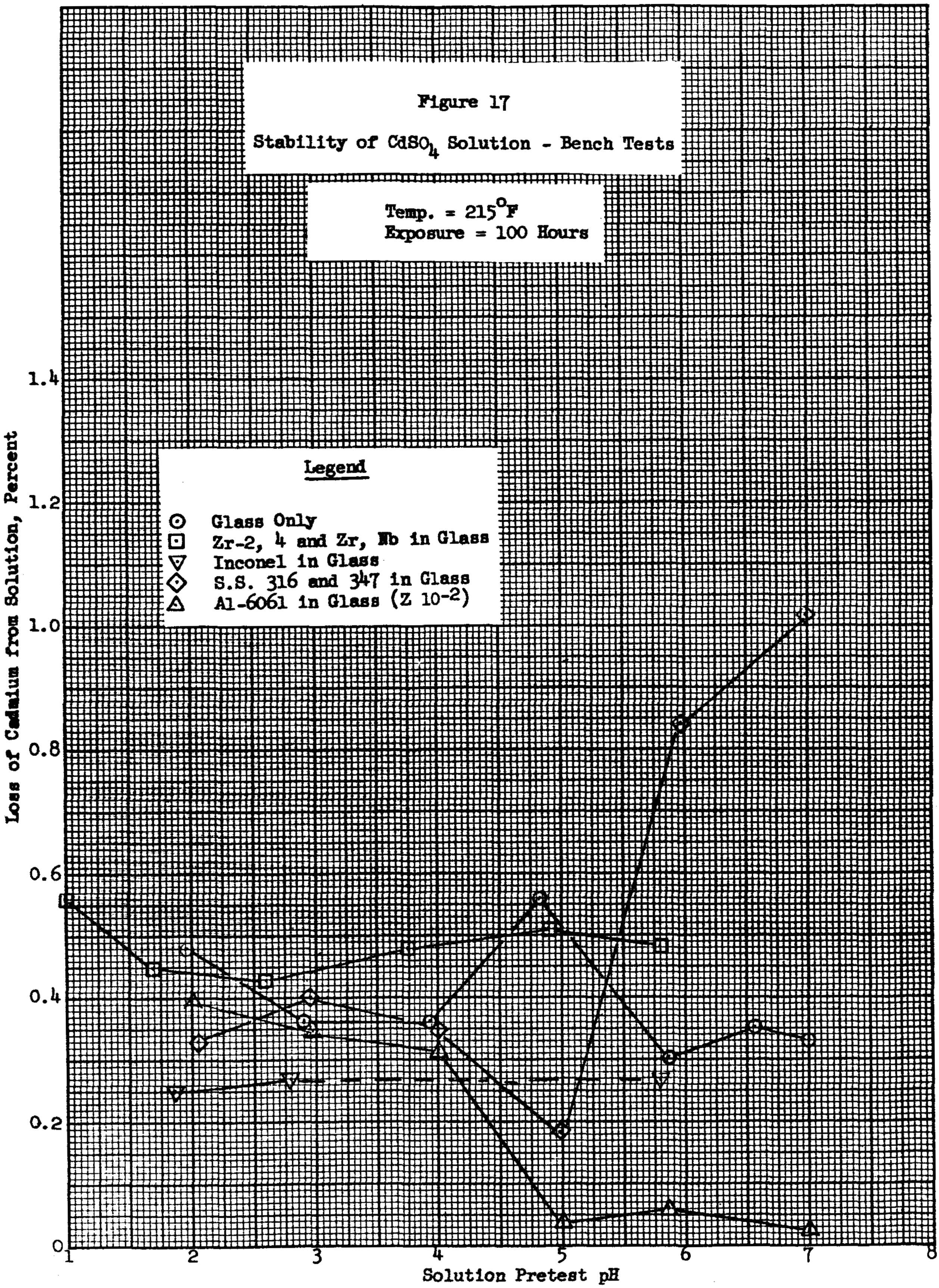


Figure 17
Stability of $CdSO_4$ Solution - Bench Tests
Temp. = 215°F
Exposure = 100 Hours
Legend
Glass Only
Zr-2, 4 and Zr, Nb in Glass
Inconel in Glass
S.S. 316 and 347 in Glass
Al-6061 in Glass (Z 10^{-2})
Loss of Cadmium from Solution, Percent
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
Solution Pretest pH

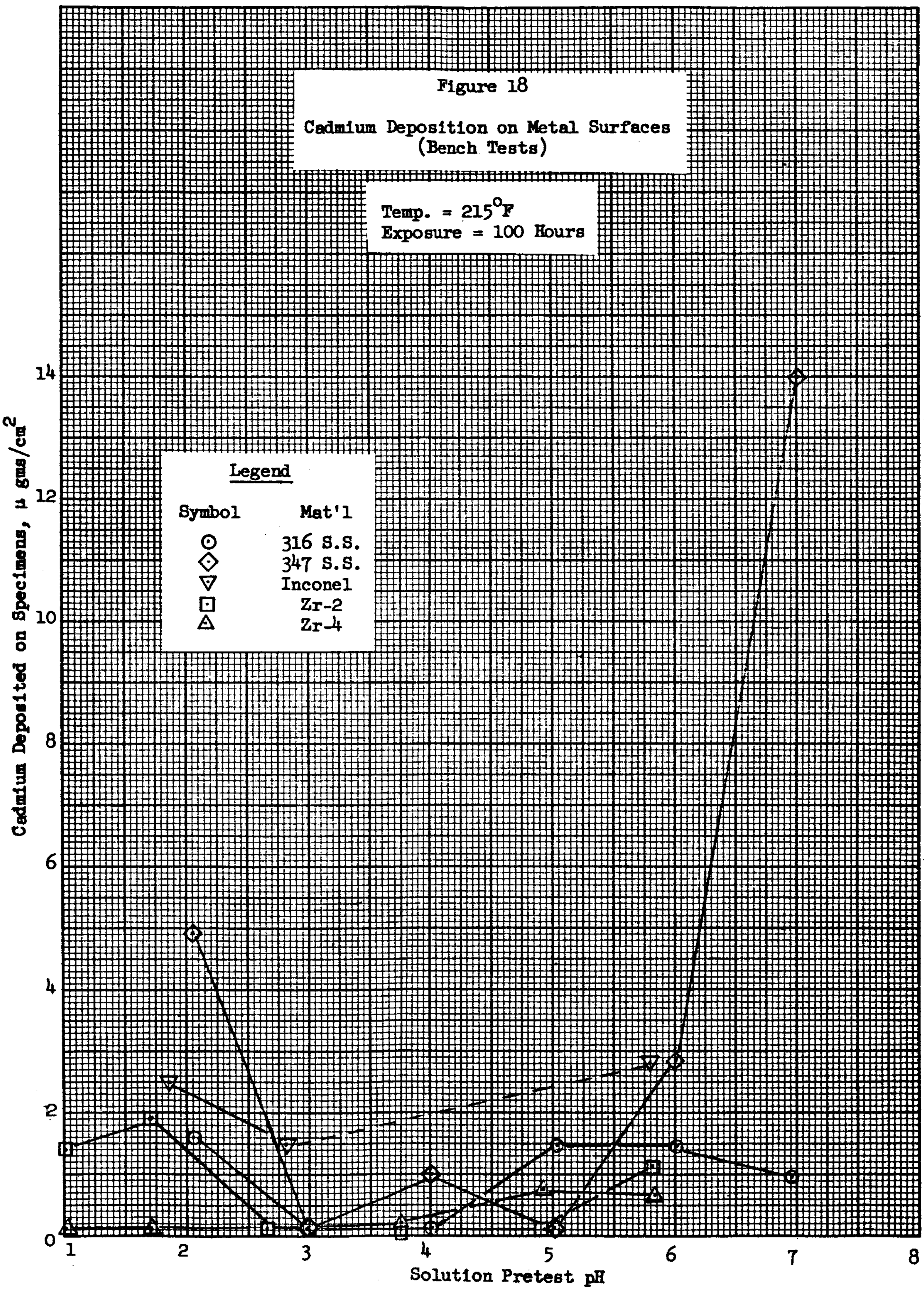


Figure 18
Cadmium Deposition on Metal Surfaces
(Bench Tests)
Temp. = 215°F
Exposure = 100 Hours
Legend
Symbol
Mat'l
316 S.S.
347 S.S.
Inconel
Zr-2
Zr-4
Cadmium Deposited on Specimens, µ gms/cm2
0
2
4
6
8
10
12
14
1
2
3
4
5
6
7
8
Solution Pretest pH

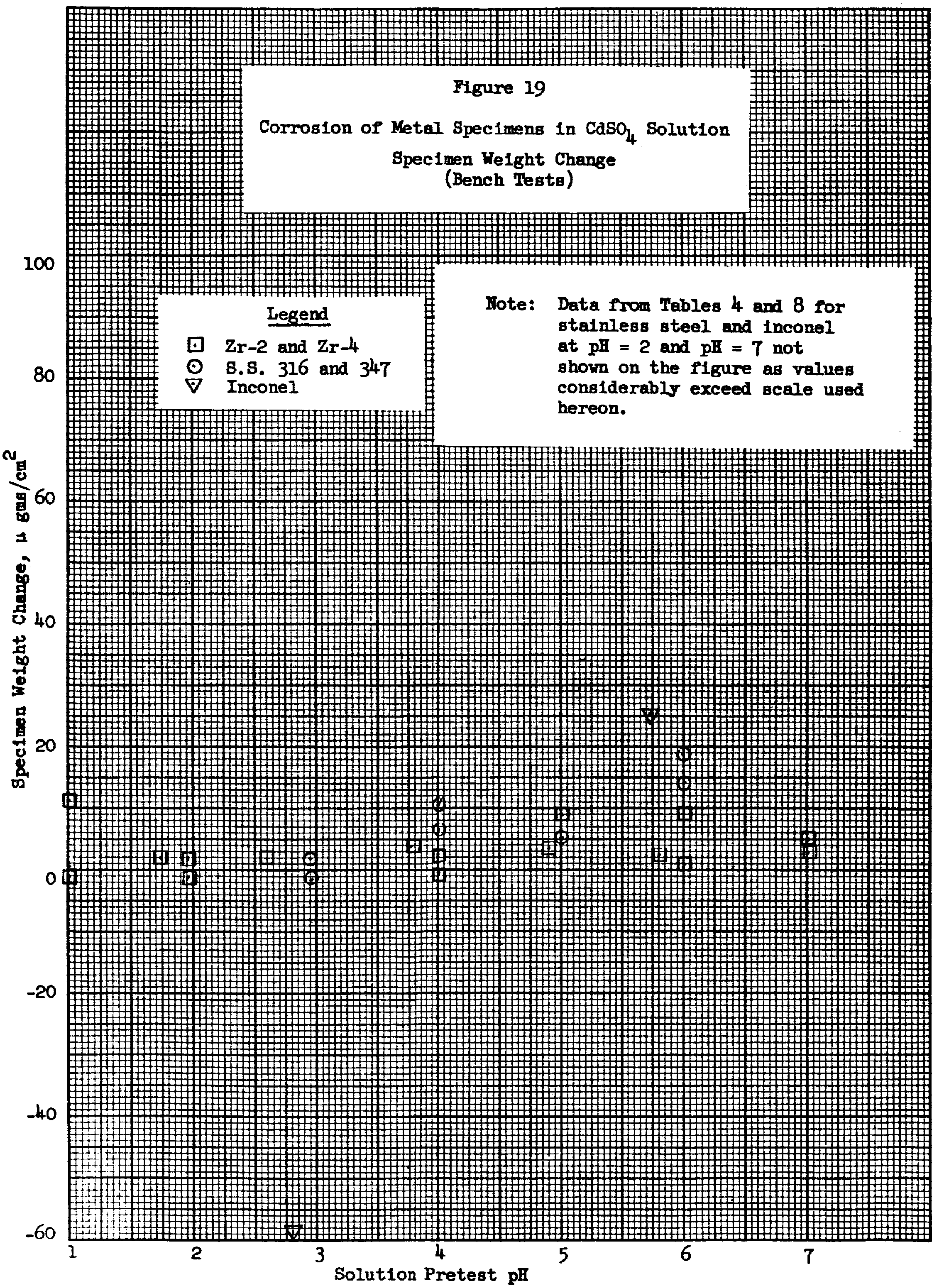


Figure 19
Corrosion of Metal Specimens in $CdSO_4$ Solution
Specimen Weight Change
(Bench Tests)
Legend
Zr-2 and Zr-4
S.S. 316 and 347
Inconel
Note: Data from Tables 4 and 8 for stainless steel and inconel at pH = 2 and pH = 7 not shown on the figure as values considerably exceed scale used hereon.
Specimen Weight Change, µ gms/cm²
100
80
60
40
20
0
-20
-40
-60
1
2
3
4
5
6
7
Solution Pretest pH

inconel is not as direct as with Zircaloy so that conclusion with respect to hydrogen generation can be made. The stainless steel and inconel specimens exhibit a tendency to gain weight as the pH is increased above 3 or 4 and to lose weight when the pH is reduced below 3 or 4. The Zircaloy specimens exhibit a slight tendency to gain weight when the pH is increased. The maximum weight gain for the Zircaloy is about 9 μgms/cm^2. This corresponds to about one-half micromole of hydrogen per square centimeter of surface area.

B. Autoclave Tests

A total of nine autoclave tests were run. The purpose of these tests was to determine (1) solution stability, (2) extent of cadmium deposition on metallic surfaces, and (3) extent of corrosion of metallic surfaces at temperatures higher than those experienced in the bench tests. Several parameters were varied during the course of the nine autoclave tests. As indicated in Tables 11 through 14, these parameters are:

1. Solution temperature
2. Solution pH
3. Time of exposure
4. Metal specimens
5. Surface area of specimens

In addition to these more obvious parameters, the effect of autoclave surface treatment and the effect of a gas-liquid interface existing in the autoclave were also investigated.

The first three tests were run with a liquid-gas interface in the autoclave. The autoclave was loaded with specimens where applicable, and partially filled with test solution plus a measured amount of demineralized water. The amount of solution was sufficient to cover the specimens at test temperature but not enough to completely fill the autoclave. There could conceivably have been a superheating effect at the autoclave wall near or at the liquid-gas interface. If this were true, the test temperature recorded by the thermocouple immersed in the test fluid could have been lower than the maximum temperature of the cadmium sulfate solution. In other words, the tests might have been more severe than is readily apparent. The test facility was modified by the addition of the accumulators shown in Figure 3 so that no liquid-gas interface existed in the remaining tests.

The autoclave internal surfaces had been wiped clean before each of the first three tests, but no attempt was made to remove the corrosion film from the autoclaves. If the surface condition or the materials in this film were contributing to the instability of the solution, this film would have to be removed. All of the autoclave internals were treated by the alkaline permanganate-citrate method before tests 4 through 7. In test 8, the autoclave internals were not pretreated for corrosion product removal. In test 9, the autoclave was first operated at 750°F and 1500 psi with steam in the autoclave to passivate the internal surfaces.

1. Solution Stability Results

The results of the first three tests described in Tables 11, 12 and 13, indicated the formation of large amounts of residues whose basic constituent was cadmium. This is shown in Table 24. The apparent gain of cadmium in Test 2 is explained by an error in measuring the cadmium concentration in the post-test solution. Tests 4 and 5 were run using the defilmed autoclaves and accumulators for control. The only difference between the two tests was the solution initial pH which was 5.3 and 4.1, respectively. The analyses showed no major improvement of solution stability under these conditions. The results are also shown in Table 24. It did appear, however, that the unadjusted pH solution, Test 4, resulted in a lower loss of cadmium than the pH 4.1 solution (Test 5) or the pH 3.4 solution (Test 3a). Even if this trend was caused by experimental and analytical inaccuracies rather than being true trends, it was obvious that there was no major improvement in solution stability as a result of lowering solution pH.

The flame analysis for cadmium in solution is accurate to within 1% of the full scale concentration. For all of the beaker tests, autoclave tests and the loop test, this concentration was 5000 ppm cadmium; therefore the accuracy of 50 ppm. Standards were checked each time samples were run, however, the curve of meter reading versus concentration was no more accurate than to within 1%. For tests where small changes of concentration were experienced, the loss of cadmium, as determined by this change could be extremely inaccurate and is therefore not used. A more accurate measure of loss of cadmium from solution would be a measure of the amount of cadmium found out of solution (i.e. - residues and deposits) as a ratio of the amount of cadmium initially present. This eliminates the necessity of considering small differences of larger numbers, and therefore improves the accuracy. The accuracies of these determinations are listed below.

Determination	Accuracy
Cadmium in a residue	± 5% relative
Impurities in a residue	± 50% relative
Impurities in a solution	± 30% relative
Cadmium in solution	± 50 ppm
Cadmium deposited on a metallic surface	(See top of page 71)

Table 24

Loss of Cadmium from Autoclave Test Solutions

Test	$\frac{\text{Cd in Residue}}{\text{Cd in Init. Soln.}} \times 100$	% Change of Cd Conc.[1]
1	-	7.67
1a	9.3	13.22
2	2.19	-1.74
3	-	1.26
3a	1.88	7.53
4	3.01	3.24
5	7.14	9.96
6	0.74	0.87
7	0.29	2.29
8	0.47*	1.55
9	1.27*	4.76

* Some additional crystalline material found adhering to specimens and specimen holder.

(1) (Cd Conc. Initial - Cd Conc. Final) 100/Cd Conc. Initial

Range of Cd Deposit, $\mu g/cm^2$	Determination Error, $\mu g/cm^2$
0.3 - 0.5	$\pm$ 0.3
1. - 2.	$\pm$ 0.5
3. - 6.	$\pm$ 1.0
10. - 15.	$\pm$ 1.5
> 15	$\pm$10% Max.

After test number 5, it was thought that the test temperature might have a meaningful effect on the solution stability. Therefore, Tests 6 and 7 were run duplicating Test 4 in every respect, with the exception that the solution temperature was reduced to 300°F and 250°F respectively. The results, listed in Tables 14 and 24, indicate a definite improvement in stability for both of these tests. However, the results do not indicate that a simple relationship exists between temperature and stability. Although the ratio of cadmium found in the residue to that present in the solution at the beginning of a test does decrease with decreasing temperature, this is not exactly the case for change of cadmium concentration in solution nor for the amount of cadmium lost from solution determined by a material balance.

Tests 8 and 9 were then run at the same conditions as Test 6, except for the condition of the autoclave internal surfaces. Test 6 was operated with an autoclave that had been precleaned by the alkaline permangate-citrate method. This autoclave was then used for Test 8, leaving any film that had formed during the previous test in tact. The autoclave used for Test 9 was first operated at 750°F and 1500 psi with steam in the autoclave in order to passivate the internal surfaces. Comparison of results between these three tests indicate that opposite trends than had been expected. The change of cadmium concentration and the cadmium lost from solution, indicate greater instability going from clean surfaces to passivated surfaces. This is shown below:

Test	Surface Condition	% Change of Cd Conc.	Loss of Cd from Soln, %
6	Pre-Cleaned	0.87	0.01
8	Once Used	1.55	2.14
9	Passivated	4.76	8.09

Enough information had been gathered during the first few autoclave tests along with that gathered during the bench study program, to realize that extensive testing of the structural material was no longer required.

Spectrographic analyses of all of these residues plus those not yet discussed, resulted in the composition listed in Table 11 through 14. All residues had high cadmium content varying between 55% and 84%. These analyses indicated that the residue might be $Cd(OH)_2$ in which the cadmium weight percent is 76.7% or CdO, whose weight percent cadmium is 87.5%.

To confirm this X-ray diffraction patterns were run of some of the residues and a sulfate analysis. The X-ray diffraction patterns, obtained from two independent sources, could not be traced to any cadmium bearing compound listed in the National Bureau of Standards Power Diffraction Index. In fact, the patterns appeared not to fit any of those listed in the index.

Remy in "Treatise on Inorganic Chemistry, Volume II"(3) discusses the basic cadmium and zinc salts which behave similarly. Although he states that little is known of the basic cadmium sulfate, his discussion of the basic cadmium chlorides and nitrates, and the basic zinc chlorides, nitrates and sulfates, indicated the strong possibility that this was being formed in these tests.

In his treatise, Remy states that the basic cadmium salts are known to possess simple layer lattices. The composition is known to vary for example from $CdSO_4 \cdot Cd(OH)_2$ to at least $Cd(SO_4)3Cd(OH)_2$. "The particular basic salt formed depends upon the concentration and pH of the solutions from which cyrstallization occurs, and also on the age of the precipitate, the immediate products of precipitation are often really not stable under the conditions of formation, but subsquently undergo transformation into the stable substances".

In addition, mixed basic salts are known to be formed with materials such as iron and copper. These salts are also layer lattice compounds and may be found within the basic sulfate salt, mixed in various proportions.

Other investigators found that the precipitate formed when cadmium sulfate solution is titrated with sodium hydroxide was $CdSO_4 \cdot 3\ Cd(OH)_2 \cdot xH_2O$.

Based upon this information, and armed with the spectrographic analysis and the chemical analysis for sulfate present in the residues to autoclave tests 1, 2 and 3, it was calculated that the basic cadmium sulfate salt formed from these tests had the formulas shown below:

Test	Calculated Ratio of $CdSO_4:Cd(OH)_2$
1	1 : 3.25
2	1 : 1.7
3	1 : 6.2

There is presently insufficient information available regarding the formation of these salts and the effect of test environment on their formation, to postulate how to prevent their forming. However, some of the parameters varied during the autoclave tests have been plotted against the results in an attempt to gather this information. Some of these comparisons are shown in Figures 20 through 29.

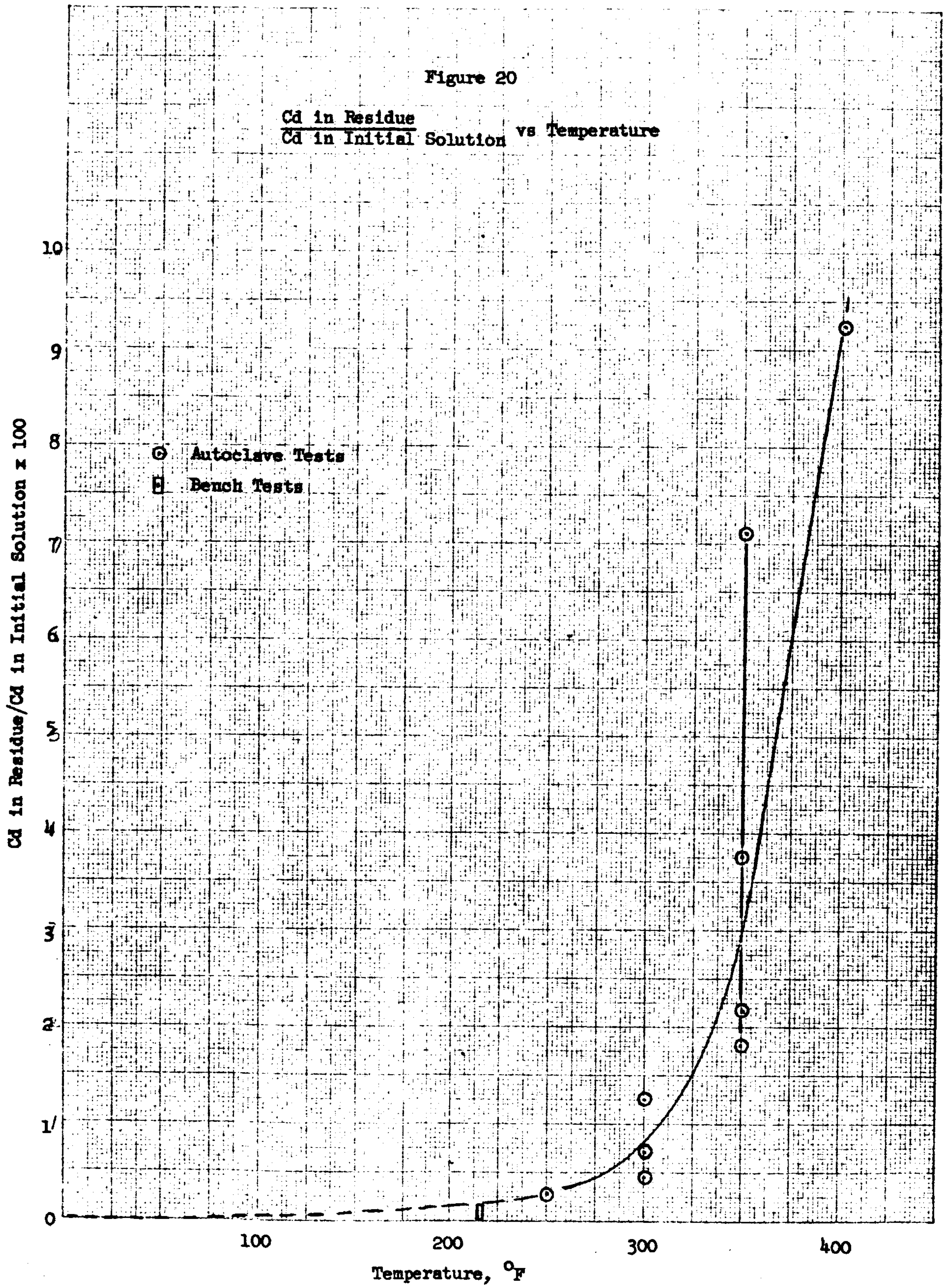


Figure 20
Cd in Residue / Cd in Initial Solution vs Temperature
Autoclave Tests
Bench Tests
Cd in Residue/Cd in Initial Solution x 100
0
1
2
3
4
5
6
7
8
9
10
100
200
300
400
Temperature, °F

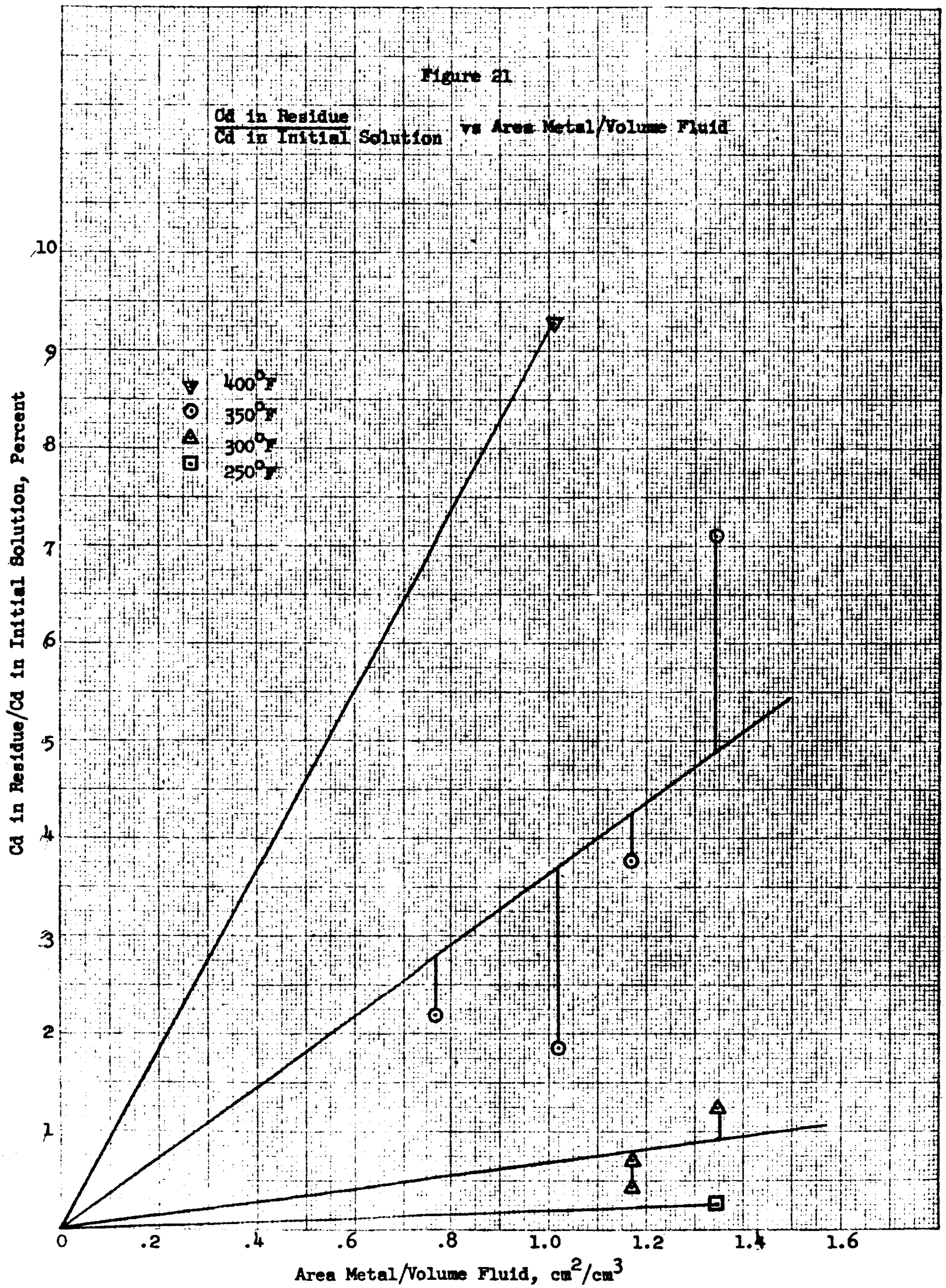


Figure 21
Cd in Residue / Cd in Initial Solution vs Area Metal/Volume Fluid
400°F
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
Area Metal/Volume Fluid, cm²/cm³
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1
2
3
4
5
6
7
8
9
10

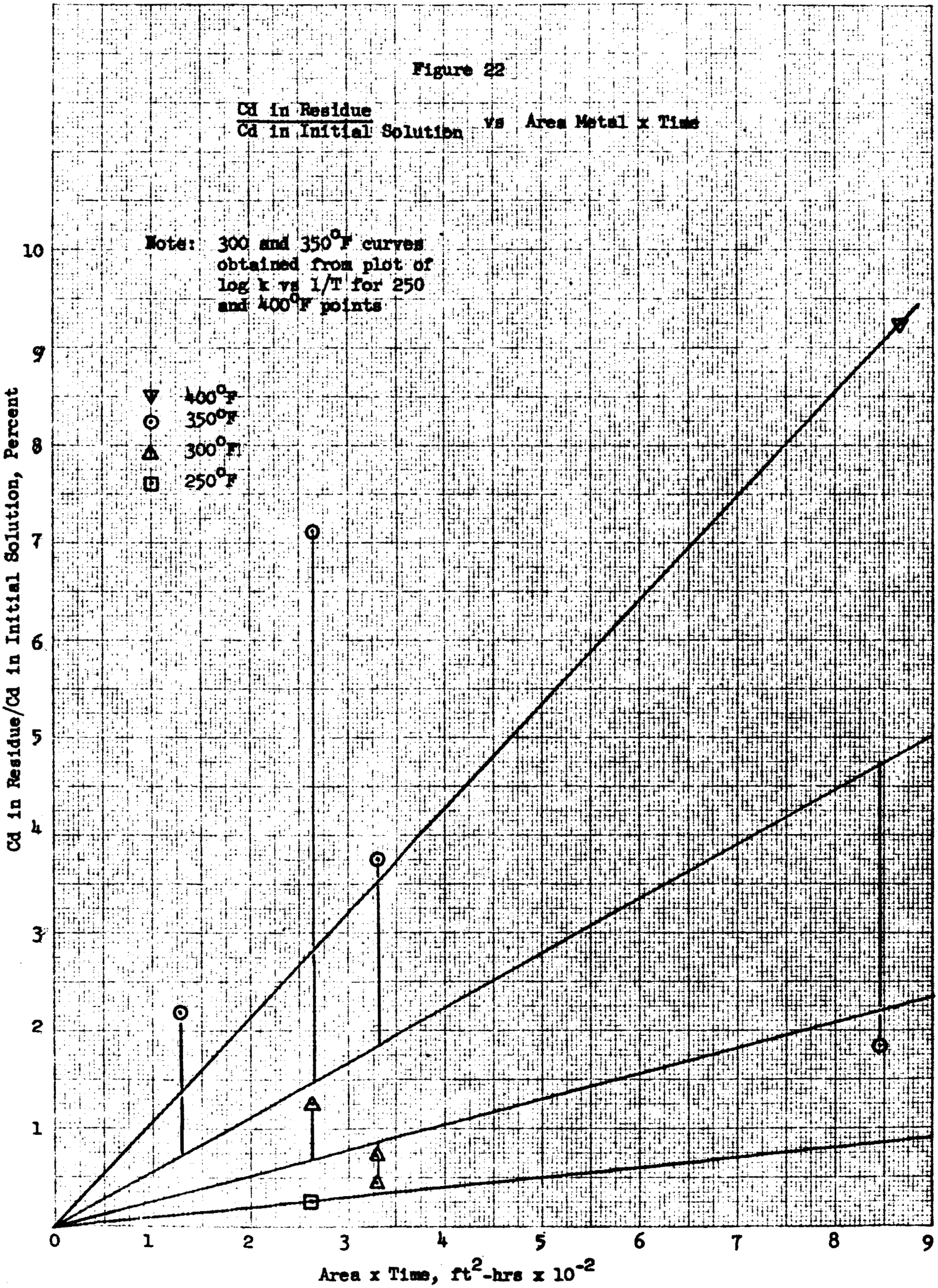


Figure 22
Cd in Residue / Cd in Initial Solution vs Area Metal x Time
Note: 300 and 350°F curves obtained from plot of log k vs 1/T for 250 and 400°F points
400°F
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
Area x Time, ft2-hrs x 10-2
0
1
2
3
4
5
6
7
8
9
10

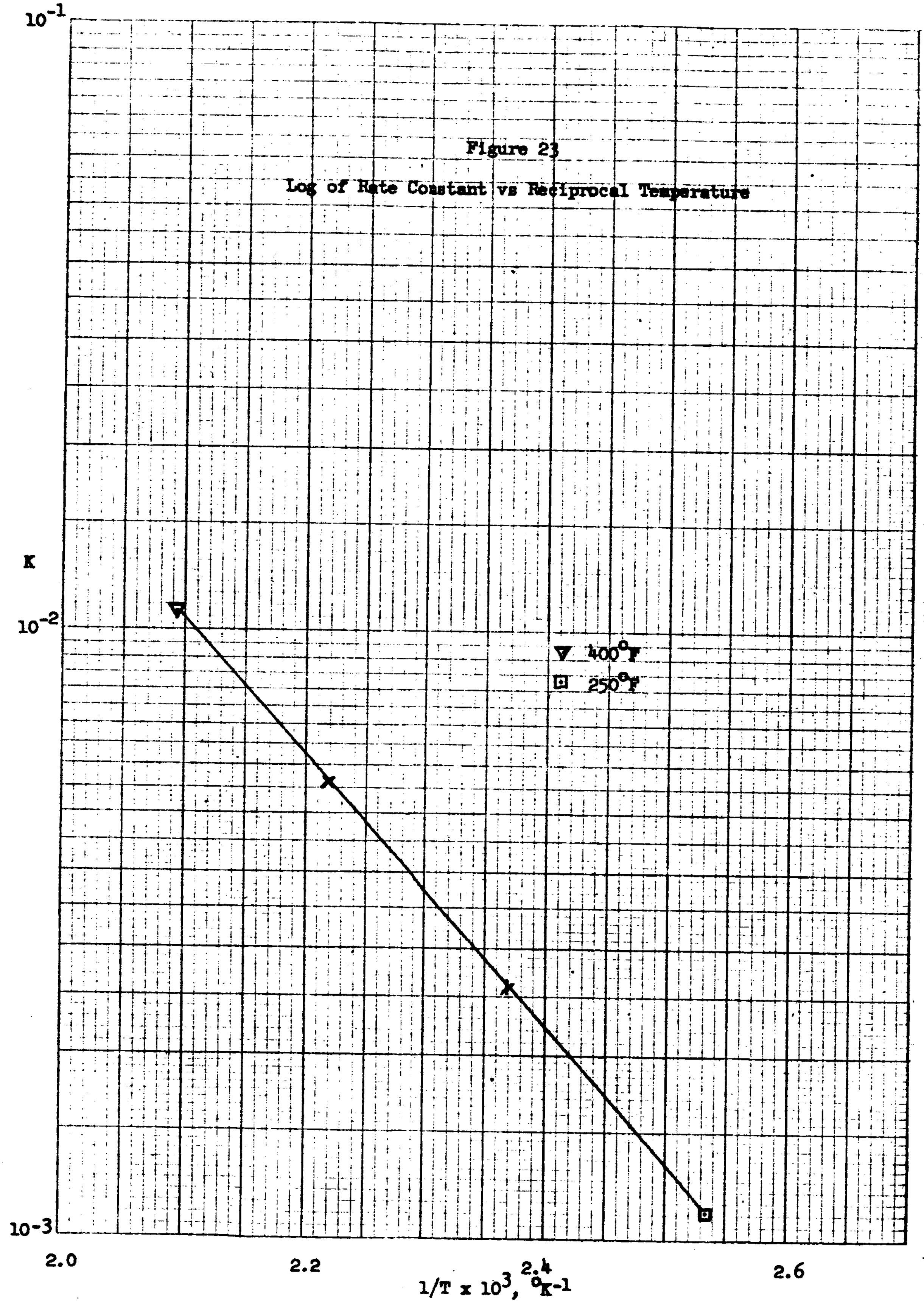


Figure 23
Log of Rate Constant vs Reciprocal Temperature
10^{-1}
K
10^{-2}
10^{-3}
▽ 400°F
⊡ 250°F
2.0
2.2
2.4
2.6
1/T x 10^3, °K-1

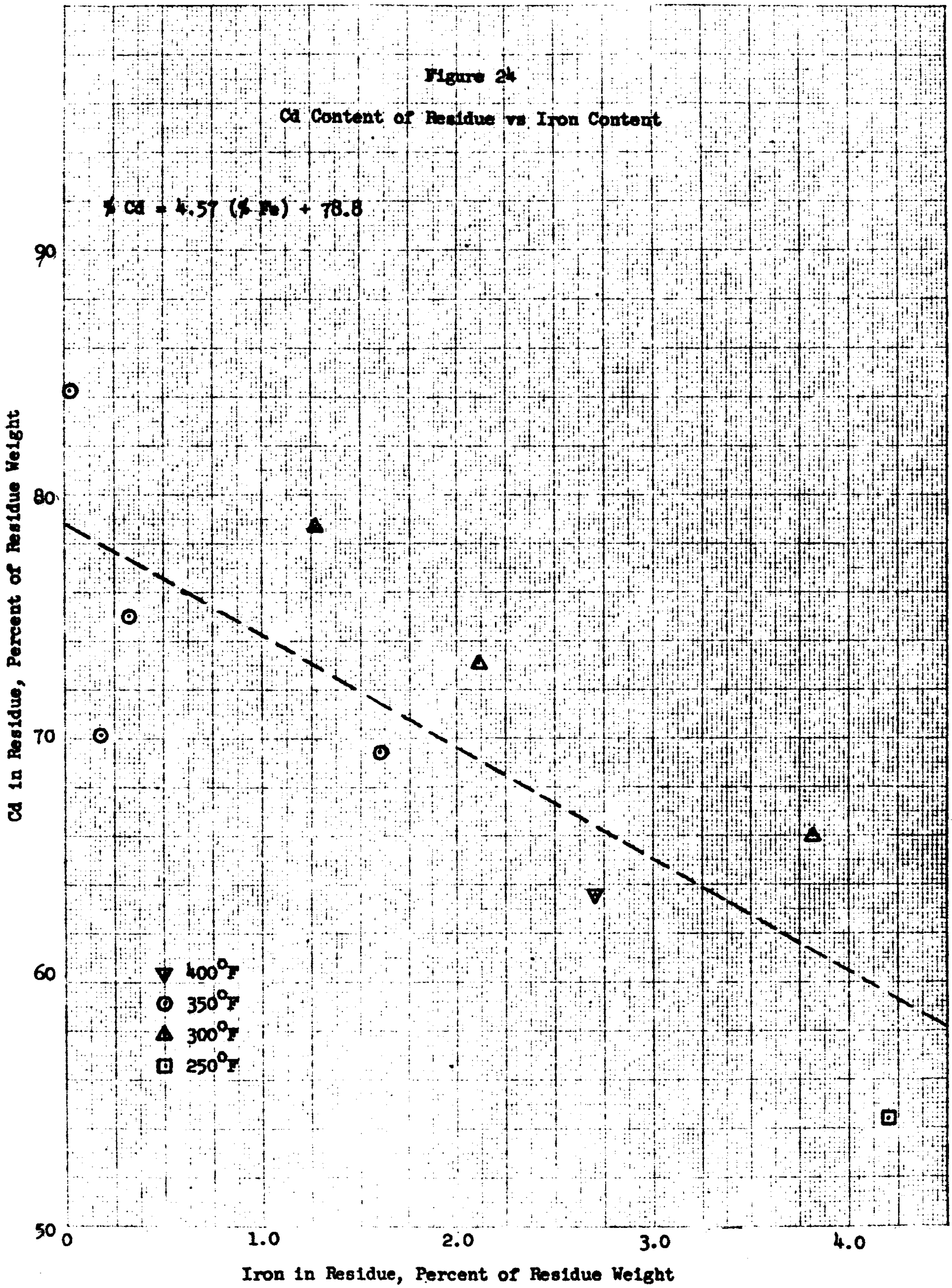


Figure 24
Cd Content of Residue vs Iron Content
% Cd = 4.57 (% Fe) + 78.8
Cd in Residue, Percent of Residue Weight
Iron in Residue, Percent of Residue Weight
90
80
70
60
50
0
1.0
2.0
3.0
4.0
400°F
350°F
300°F
250°F

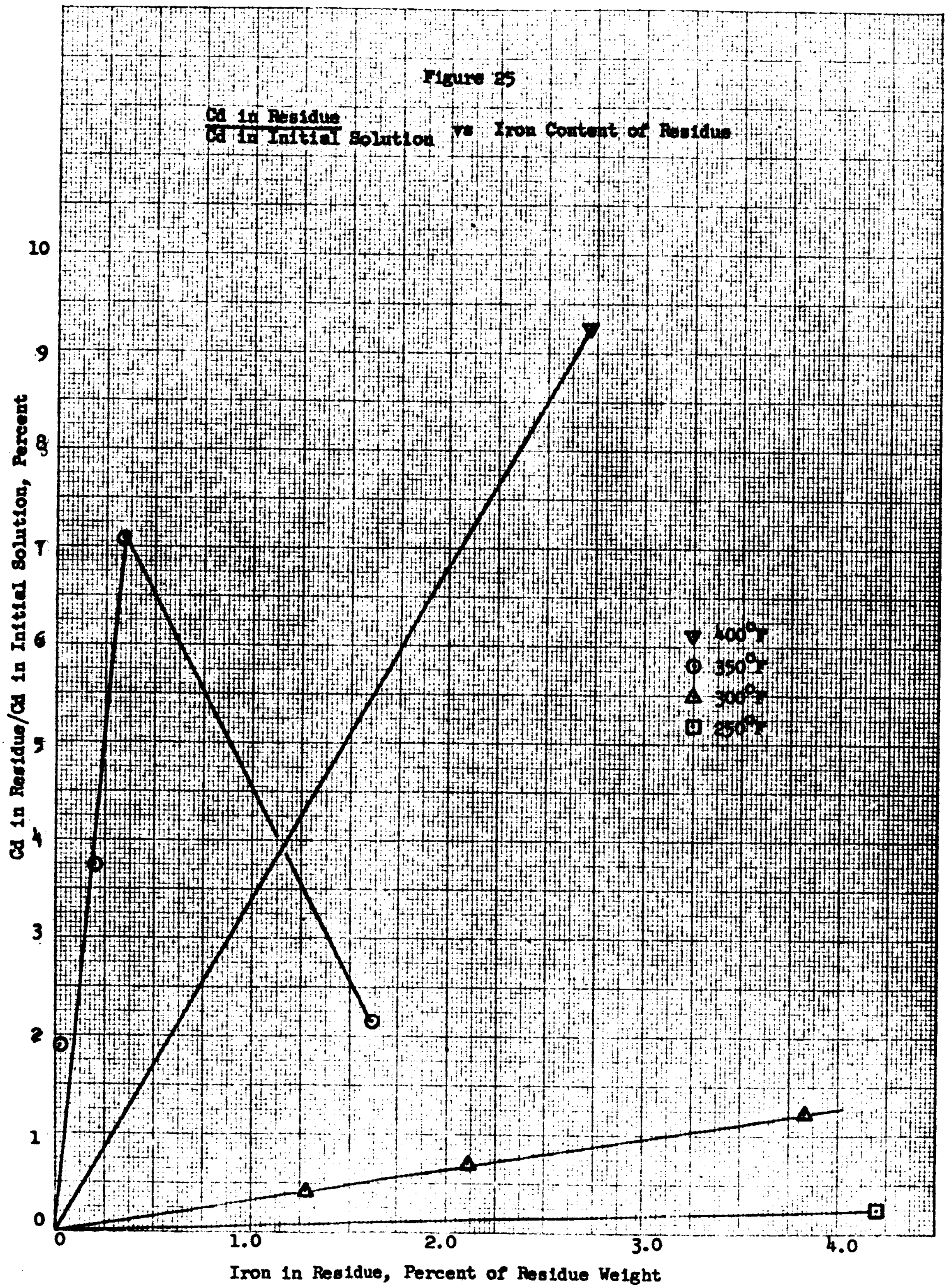


Figure 25
Cd in Residue / Cd in Initial Solution vs Iron Content of Residue
400°F
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
Iron in Residue, Percent of Residue Weight
0
1
2
3
4
5
6
7
8
9
10
1.0
2.0
3.0
4.0

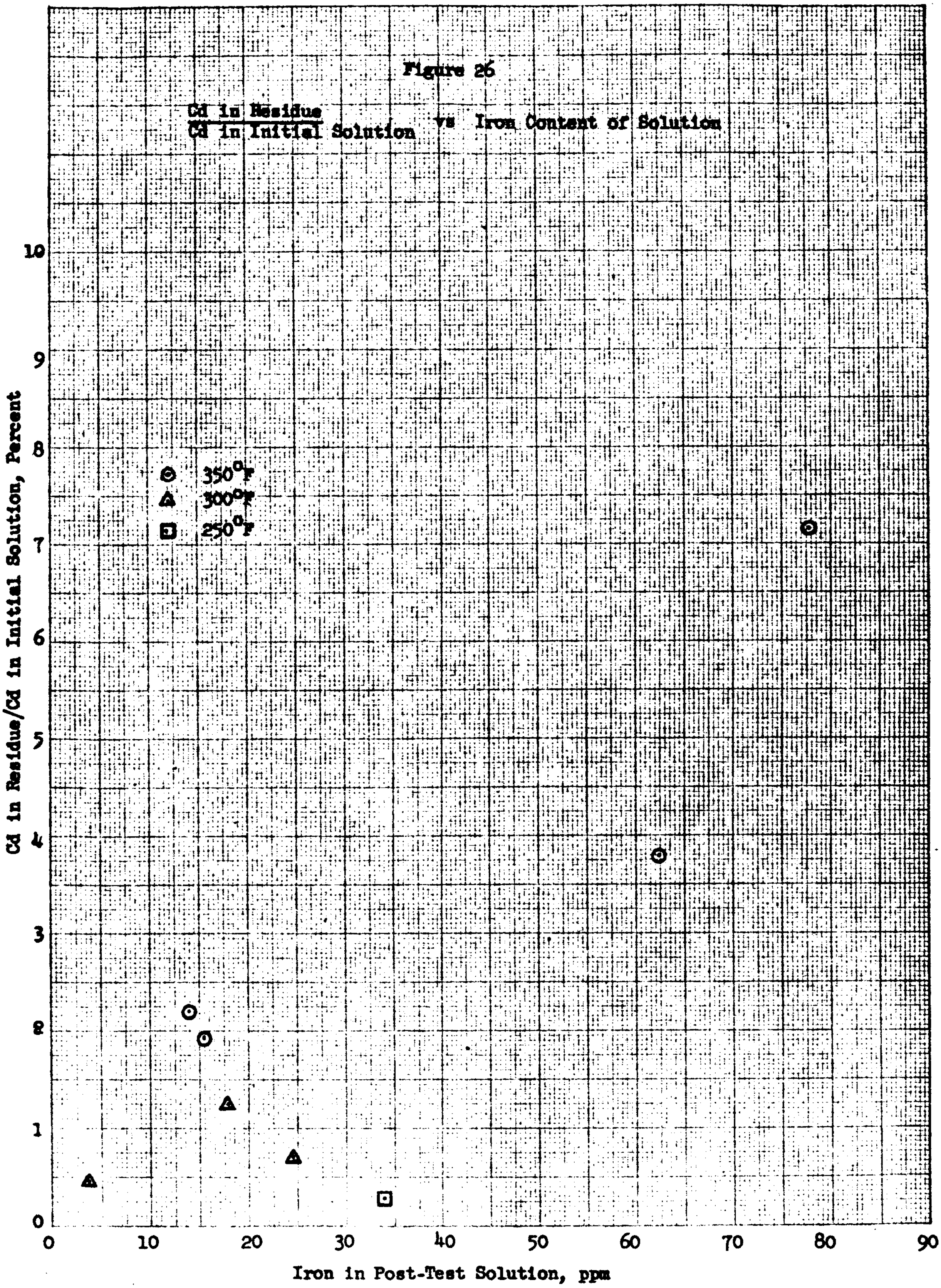


Figure 26
Cd in Residue / Cd in Initial Solution vs Iron Content of Solution
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
Iron in Post-Test Solution, ppm
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90

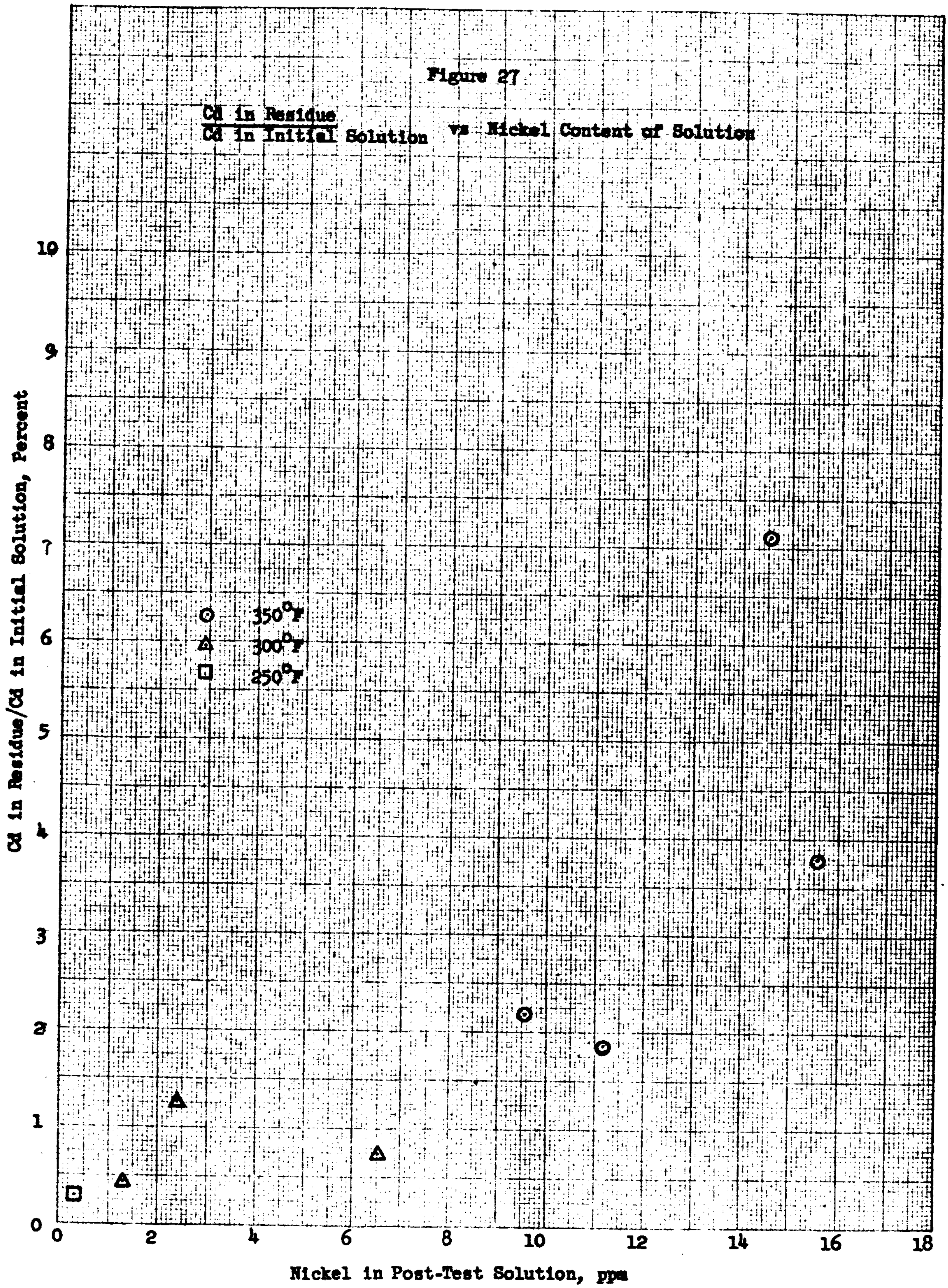


Figure 27
Cd in Residue / Cd in Initial Solution vs Nickel Content of Solution
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10
12
14
16
18
Nickel in Post-Test Solution, ppm

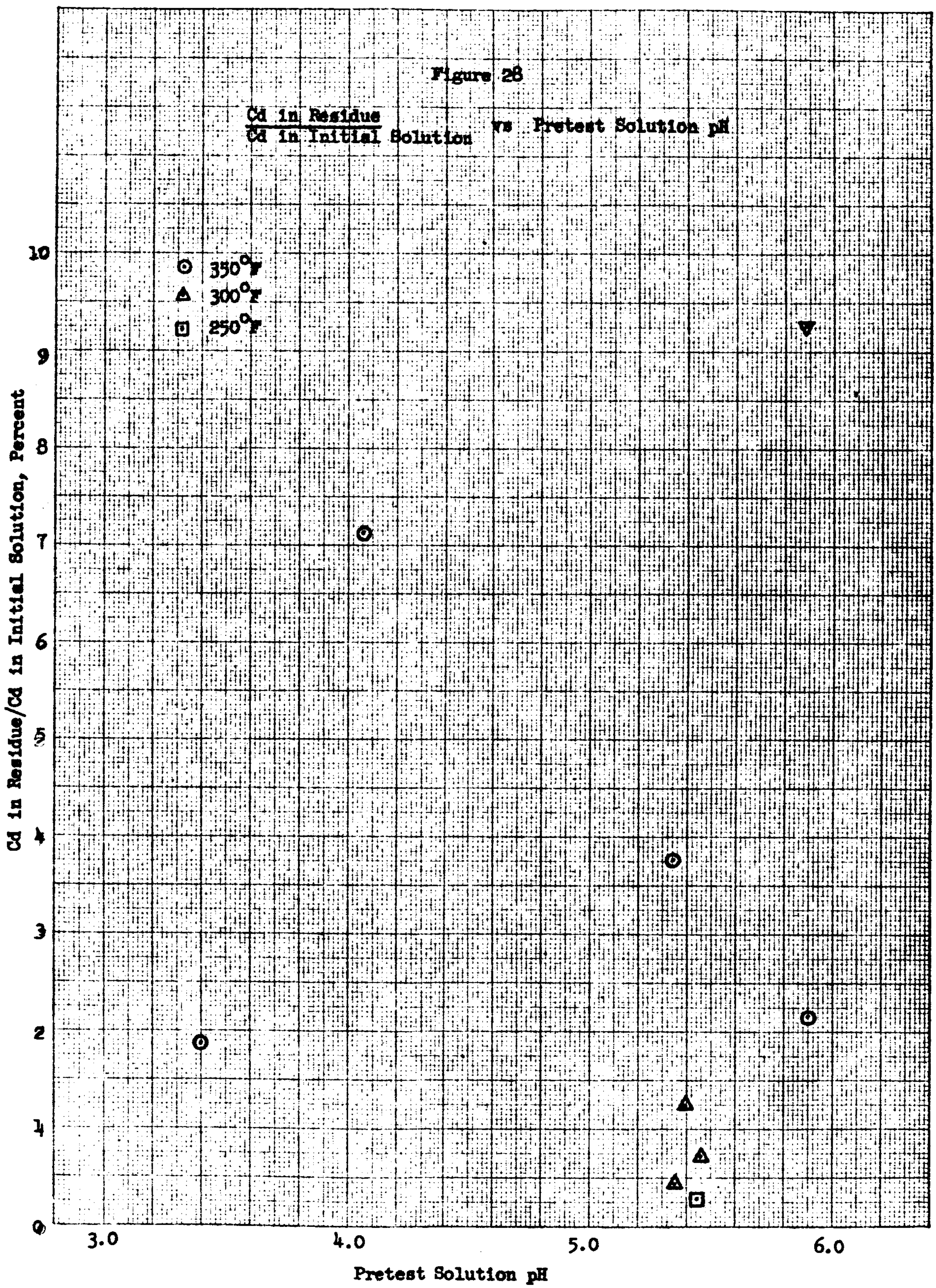


Figure 28
Cd in Residue / Cd in Initial Solution vs Pretest Solution pH
350°F
300°F
250°F
10
9
8
7
6
5
4
3
2
1
0
3.0
4.0
5.0
6.0
Pretest Solution pH
Cd in Residue/Cd in Initial Solution, Percent

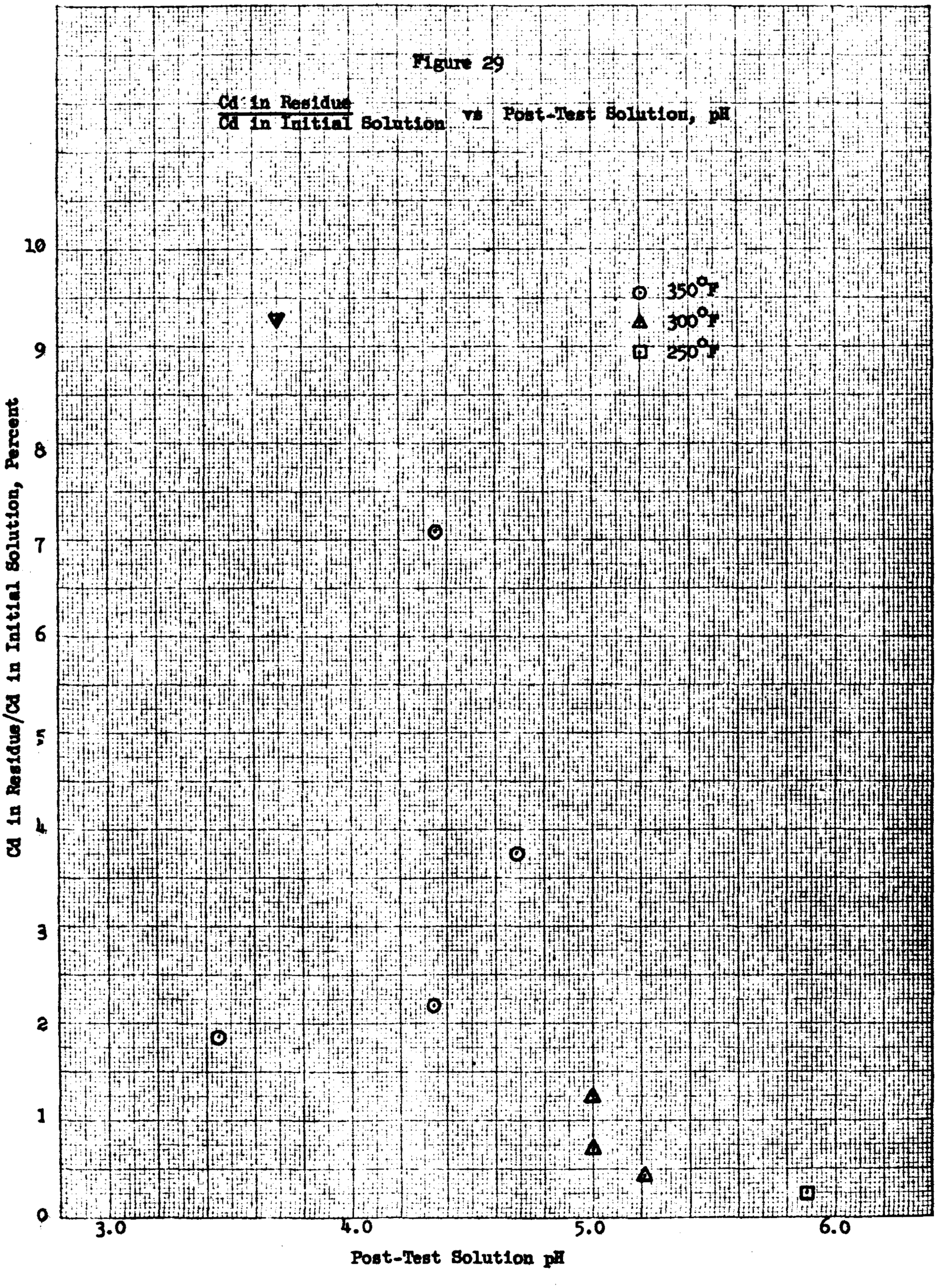


Figure 29
$\frac{\text{Cd in Residue}}{\text{Cd in Initial Solution}}$ vs Post-Test Solution, pH
350°F
300°F
250°F
Cd in Residue/Cd in Initial Solution, Percent
0
1
2
3
4
5
6
7
8
9
10
3.0
4.0
5.0
6.0
Post-Test Solution pH

Figure 20 is a plot of the ratio of cadmium found in the residue to the cadmium initially present in solution versus test temperature. The points plotted are for all of the tests. Tests 1a and 3a were operated for 500 hours, all others for 100 hours.

In an attempt to relate the solution stability with the surface area/volume ratio, Figure 21 was drawn. There are possible trends which require further study. The effect of temperature has already been shown. If the area of metal in contact with solution is to be of some effect, it would seem that test duration would also effect the results, since all catalytic reactions are dependent on rate. If the loss of cadmium from solution were described by:

$$\frac{dCd}{dt} = - KA_M Cd$$

where dCd/dt is the rate of change

A_M is the metal surface area

Cd is the cadmium concentration at any time

K is the rate constant

rearranging and integrating

$$\frac{Cd}{Cd_I} = e^{-K A_M t}$$

The fractional change of concentration can be expressed as

$$\frac{Cd_I - Cd}{Cd_I} = 1 - \frac{Cd}{Cd_I} = 1 - e^{-K A_M t}$$

Using only the first term of the expansion as being significant:

$$\frac{Cd_I - Cd}{Cd_I} = \approx K A_M t$$

As explained earlier, the measure of change of cadmium concentration can be inaccurate. The cadmium found out of solution should be a measure of the loss from solution. Therefore:

$$\frac{\text{Cd in Residue}}{\text{Cd in Init. Soln.}} = K A_M t$$

Figure 22 is a plot of this ratio versus the metal area times the test duration. Lines were drawn only for the 250 and 400°F points. These slopes should be the same rate constant as determined by the Airbenius equation:

$$K = Be^{-\Delta E/RT}$$

where ΔE is the activation energy

T is the absolute temperature

R is the universal constant, 1.9872 cal/mol °R

This equation is a straight line on semi-log paper when log K is plotted against $\frac{1}{T}$ and its slope is $-\Delta E/R$. The slopes of the 250 and 400°F lines on Figure 22 were plotted in Figure 23. The slopes of the 300 and 350°F lines were picked off and the appropriate lines drawn on Figure 22. They seem to be approximately in the correct position. From Figure 23, the activation energy was calculated to be 4.45 K-cal/mole. This value is in line with activation energies required for surface type reactions where diffusion to or adsorption onto the surface is controlling.

In another attempt to establish that a reaction is occurring at the surface, and that the surface, in this case, stainless steel, was entering the reaction, the iron content of the residues of the autoclave tests was plotted against the cadmium content of the residues. This is shown in Figure 24. Line drawn and its equation was determined using "the method of least squares" and rejecting none of the points. No explanation of this apparent trend is available. Figures 25, 26, and 27 were also drawn in an attempt to correlate a cadmium instability with the metal container. No trends are apparent from these figures.

Two other figures were drawn, 28 and 29, this time trying to connect the instability with solution pH, both pretest and post-test. No correlation is evident from these two figures.

In summary, the autoclave tests prove that corrosion of the reference materials is not severe at temperatures up to 400°F for durations up to 500 hours. They also showed that the solution stability is dependent upon temperature; being quite unstable at 350°F and above, with questionable stability at 250°F and 300°F. This stability seemed to be independent of solution pH. The test results indicate that a relationship exists between stability and the area of containing metal exposed to solution.

2. Cadmium Deposition Results

The cadmium deposited on the stainless steel and Zircaloy specimens in Tests 1 and 3 are plotted in Figures 30 and 31. For a solution temperature of 400°F and pH of 5.88, the cadmium deposition on Zircaloy is less

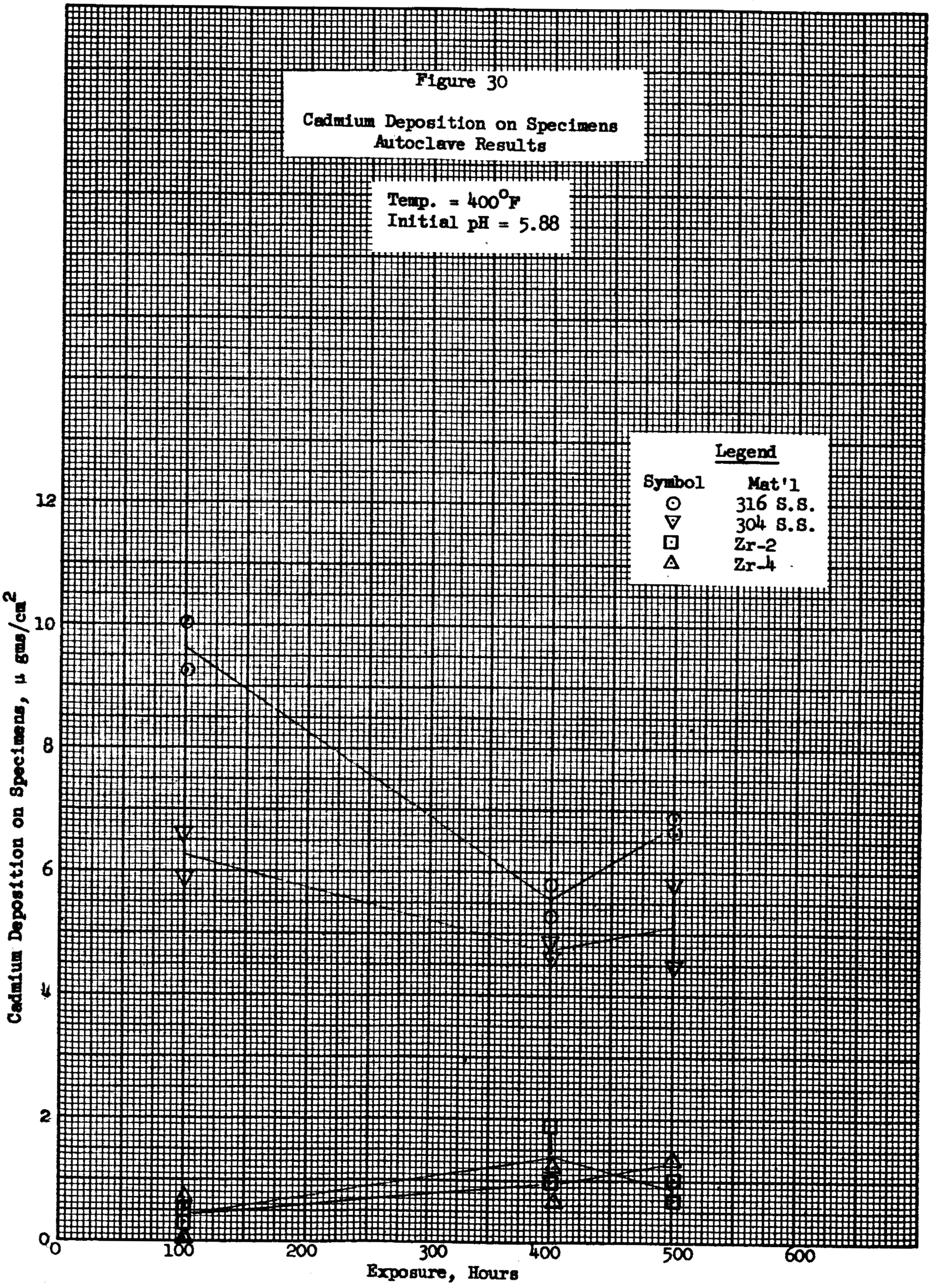


Figure 30
Cadmium Deposition on Specimens
Autoclave Results
Temp. = 400°F
Initial pH = 5.88
Legend
Symbol
Mat'l
316 S.S.
304 S.S.
Zr-2
Zr-4
Cadmium Deposition on Specimens, µ gms/cm²
0
2
4
6
8
10
12
0
100
200
300
400
500
600
Exposure, Hours

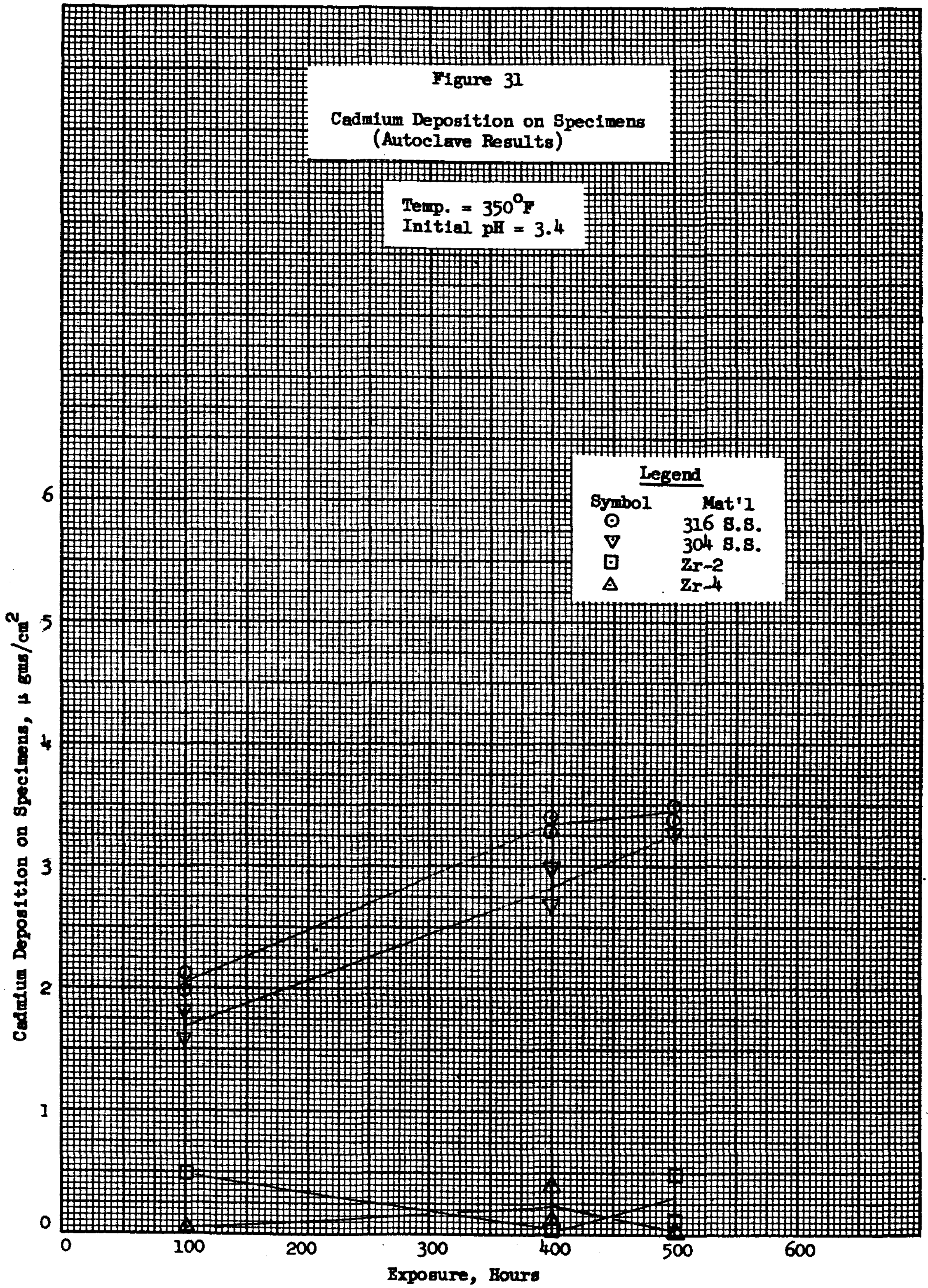


Figure 31
Cadmium Deposition on Specimens
(Autoclave Results)
Temp. = 350°F
Initial pH = 3.4
Legend
Symbol
Mat'l
316 S.S.
304 S.S.
Zr-2
Zr-4
Cadmium Deposition on Specimens, μ gms/cm²
0
1
2
3
4
5
6
0
100
200
300
400
500
600
Exposure, Hours

than that on stainless steel. After 500 hours exposure, the deposition on Zircaloy is about 1 $\mu gm/cm^2$ and the corresponding deposition on stainless steel specimens was between 4.5 and 7 $\mu gms/cm^2$. The cadmium deposition appears to increase with exposure on the Zircaloy samples. It appears to decrease and then increase with exposure on the stainless steel specimens. This anomaly could be due to experimental error.

The third test series was conducted at a temperature of 350°F and pH of 3.4. In this test, the cadmium deposition is still greater on the stainless steel specimens than on the Zircaloy specimens. The cadmium deposition on both the stainless steel and the Zircaloy specimens is less for this test series than for the higher temperature and pH tests.

3. Corrosion Results

Corrosion rates for the materials of interest as well as the cadmium deposition on these materials had been adequately examined at the temperatures, solution chemistries, and durations of interest in the first few autoclave tests. However, it was considered desirable not to change the ratio of the surface area of exposed metal to volume of test fluid for any of the remaining tests. Therefore, in all tests starting with number four, Metal Area/Soln. Vol. varied by no more than 15% from test to test. These specimens were neither weighed, dimensionally checked, nor checked for cadmium deposition. Occasionally, one small specimen was inserted in a test for a corrosion check.

The 316 stainless steel specimens from Tests 1 and 3 were stripped by the alkaline permanganate-citrate method to obtain total metal attack. These results are plotted in Figure 32 and show a leveling off of corrosion rate with time. The hydrogen evolution caused by this corrosion is correspondingly reaching a steady state value, and can be calculated from the equation:

$$3\ Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

The corrosion of the zirconium alloys is shown in Figure 33. It has been found that zirconium oxidation follows the equation:

$$Zr + 2H_2O \longrightarrow ZrO_2 + 2H_2$$

Based upon this reaction and the experience which says that this oxide film will adhere to the base metal, 1 mg/dm^2 specimen weight increase will result in the formation of 1.4 cc of hydrogen (at STP) per dm^2 surface. Zircaloy corrosion studies further indicate that for Zircaloy-2, 55% of this hydrogen will hydride with the base material with the remaining 45% released as molecular hydrogen to the solution. The hydrogen retention in Zircaloy-4 is 30% while the anticipated retention in the zirconium-2-1/2% niobium alloy is 10%.

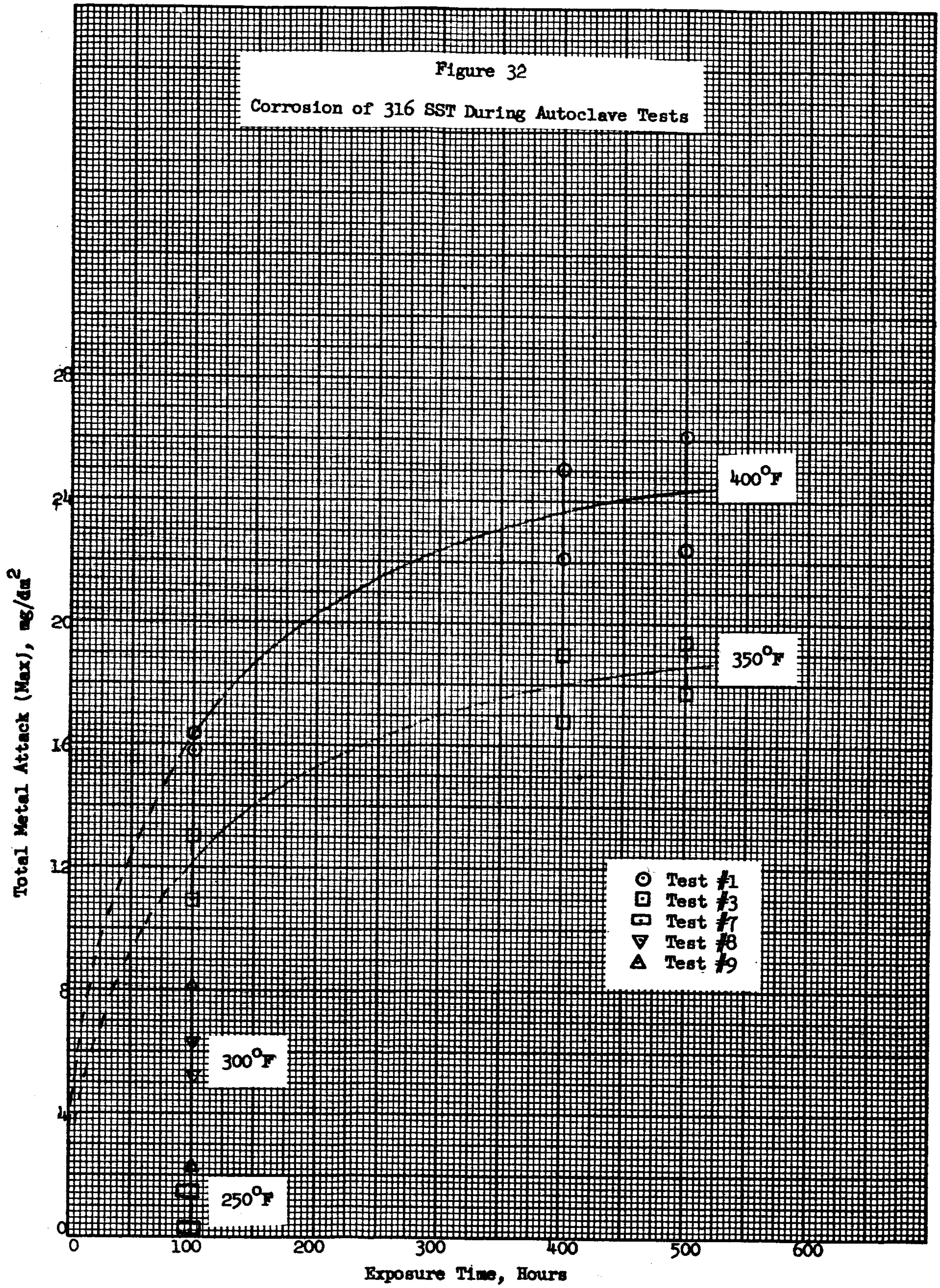


Figure 32
Corrosion of 316 SST During Autoclave Tests
400°F
350°F
300°F
250°F
Test #1
Test #3
Test #7
Test #8
Test #9
Total Metal Attack (Max), mg/dm²
Exposure Time, Hours
0
4
8
12
16
20
24
28
0
100
200
300
400
500
600

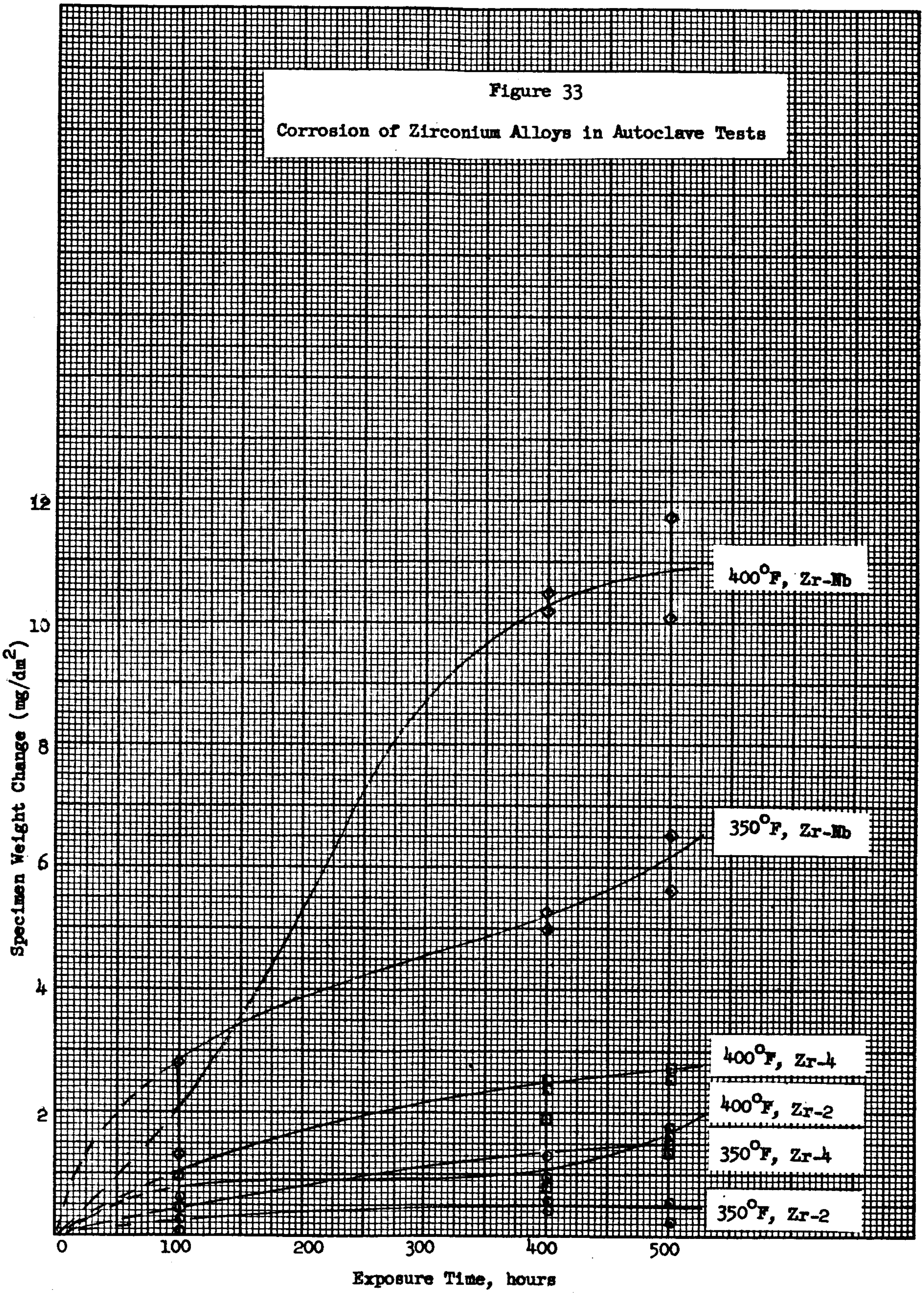


Figure 33
Corrosion of Zirconium Alloys in Autoclave Tests
12
10
8
6
4
2
0
100
200
300
400
500
Specimen Weight Change (mg/dm²)
Exposure Time, hours
400°F, Zr-Nb
350°F, Zr-Nb
400°F, Zr-4
400°F, Zr-2
350°F, Zr-4
350°F, Zr-2

C. Loop Test

The loop tests were run to determine the effect of heat flux and fluid velocity on the compatibility between $CdSO_4$ solution and the structural materials of interest.

The effect of the test conditions and environment on the solution is quite obvious from the discussion and associated tables appearing in a previous section. The cadmium concentration at the end of the test was 8.8% lower in the loop, where the temperature was maintained at 350°F, and 15.4% lower in the makeup tank where the solution was boiling continuously at atmospheric pressure, than the 24 hr. concentrations. It must be realized that there was a certain amount of mixing of the two systems during the test due to the normal fluctuations of loop temperature and pressure causing intermittent makeup and letdown. In addition, the material balance performed after collecting all of the solution and analyzing for cadmium, showed that 19.8% of the cadmium had left solution, with 18.6% remaining unaccounted for after all analyses were complete and only 1.23% collected in the various residues.

The test was originally planned to be operated in a pH range of 3.5-4.0. However, a small excess of sulphuric acid was added at the beginning of the test, with a resulting pH of about 2.8. This difference was not deemed significant enough to warrant delaying the test, which went ahead as scheduled.

Other than the change of cadmium concentration, the only solution quality which changed as the test progressed, was the chloride content. The only logical explanations for this are that some chloride bearing materials could have been adhering to the loop and/or component internal surfaces and was dissolved or leeched off by the acid solution, or, that the continual boiling away of the makeup tank water coupled with continual makeup to the tank from a demineralized water source, in order to maintain constant level, could have concentrated the small amounts of chloride impurities. Standard samples containing representative amounts of cadmium concentrations, chloride concentrations and pH, were made and analyzed to determine if this mixture could be analyzed accurately using the standard techniques. These checks were readily analyzed accurately.

The heat flux across the specimen-solution interface remained constant at 75,000 Btu/hr. ft.^{2} within 5% for the test duration, except for the 17 hr. period during the first night, when it was manually reduced to 65,000 Btu/hr. ft.^{2} to prevent any trips of the system. The test heater power was tripped off prior to this and again near the end of the test. These trips were traced to the pressure differential measuring device which could trip the power if the ΔP of the solution following in the test section housing dropped below a preset value. This was a safety device originally intended to prevent continued heating if solution flow stopped. However, the location of the makeup pump in the system, was such that a stroke of this pump could produce a momentary back pressure at the instrument in question, thereby reducing the ΔP and causing the trip.

At the end of the test, the various solutions collected were filtered, with most residues and some filtrates analyzed. It is interesting to note that the residues obtained from filtering the loop fluid both with the in-line filter and from the one-gallon sample, contained considerably smaller proportions of cadmium than did those residues found adhering to, or in stagnant areas near, the heat transfer sections, namely the test heater and loop heater. The residues associated with makeup tank solution were similarly low in cadmium content. All other analyses of both residues and filtrates were similar to those obtained from autoclave tests as was the appearance of these samples.

The heat flux supplied to the cylindrical specimens had a very definite effect on the corrosion of all three materials tested; 316 stainless steel, Zircaloy-2 and Zircaloy-4. The results are summarized in Table 25 where they are also compared to the results obtained from bench and autoclave tests. Before discussing this effect, the heat transfer and fluid flow calculations will be presented so that proper comparisons can be made.

The fluid flowrate during the test was 10.7 gpm @ 350°F. With 0.815" O.D. specimens in a 1" pipe, the fluid velocity in the test section was:

$$V = 0.936\ (\text{GPM})/A_f = 10 \text{ ft/sec}$$

where V is the fluid velocity, ft/sec

GPM is the volumetric flowrate, gal per min

A_f is the cross sectional flow area, inches

The heat transfer coefficient is obtained from the Dittus-Boelter equation:

$$\frac{hD}{K} = 0.023\ (Re)^{.8}\ (Pr)^{.4}$$

At Test Conditions $Re = 1.02 \times 10^5$

$Pr = 1.02$

resulting in a film coefficient, h, of 4730 Btu/hr ft^2 °F. With a heat flux of 75,000 Btu/hr ft^2. With a heat flux of 75,000 Btu/hr ft^2 and a heat transfer area of 0.32 ft^2, the ΔT across the film is:

$$\Delta T_f = Q''/h = 75{,}000/4{,}730 = 15.9^\circ F$$

The increase of coolant temperature from inlet to outlet is given by:

$$\Delta T_c = q/WC_p = 4.8^\circ F$$

Table 25

Comparison of Weight Change Data as a Result of All Types of Tests

		316 SST(1)	Zr-2(2)	Zr-4(2)
A.	Bench Tests 215°F, 100 hours pH = 3-6	+.19 to +1.4	.15 to .32	.13 to .38
B.	Autoclave Tests 350°F, 100 hours pH = 3.4	5.8 to 7.2	.08 to .23	-2.0 to .45
	400°F, 100 hours pH - 5.88	7.7	.66 to .99	.98 to 1.00
C.	Loop Tests 350°F, 90 hours pH = 3			
1.	Velocity Holder	3.4(3)	2.8(4)	4.5(4)
2.	Ends of Heater	4.0(3)	7.0(5)	14.0(5)
3.	On Heater Element	12.0(3)	16.0(5)	19.0(5)

Notes:

(1) All changes are losses except where otherwise indicated.

(2) All changes are gains except where otherwise indicated.

(3) Average of weight change values using entire surface area of samples.

(4) Value at 10'/sec velocity using only area of sample exposed to flow.

(5) Average of weight change values using the entire area of sample exposed to flow.

where q is the heat transferred, Btu/hr

W is the mass flowrate, lb/hr

C_p is the fluid specific heat, Btu/lb, $^{\circ}F$

Therefore, near the bottom end of the heater, where the bulk fluid temperature is 350°F, the specimen surface temperature was 366°F, and near the top of the heater, the bulk temperature was 355°F and the surface 371°F.

A check was made to insure that no nucleate boiling occurred at the specimen surface. The inception of nucleate boiling is when:

$$T_{Bulk} + \Delta T_{Film} = T_{Sat} + \Delta T_{Sat}$$

Boiling would occur first near the top end of the heater where the solution enthalpy is at its highest value. With an inlet temperature of 350°F, a pressure of 600 psig and a flowrate of 10.7 gpm, the heat flux required to initiate nucleate boiling is determined from:

$$T_{Bulk} = 350 + \Delta T_c = 350 + Q'' \, A/WC_p$$

$$\Delta T_{Film} = Q''/h$$

$$T_{Sat} = 488.8$$

$$\Delta T_{Sat} = 1.9 \, (Q'')^{.25} \, e^{-P/900}$$

Calculations show that this heat flux would need to be 6×10^5 Btu/hr ft^2. The resulting bulk outlet temperature would be 389°F with a specimen surface temperature of 515°F. With both the heater power constantly monitored as is the pressure and inlet and outlet temperatures, none of these extreme conditions could have existed during the test; therefore, no nucleate boiling.

1. <u>Corrosion Behavior</u>

In the discussions which follow it is assumed that weight change is related to corrosion. Examination of the information included in Tables 19, 20, and 25 indicates the following:

a. In the range of velocities from 5 to 30 ft/sec there is no effect of velocity on corrosion of stainless steel. Under these circumstances it appears advisable to compute corrosion rates based on total sample area.

b. There is a velocity effect on corrosion for zirconium alloys. The results are shown in Figure 34. Comparison of results from heated and unheated specimens should be done on the basis of maximum values at the proper velocity.

c. The agreement between values for the end of heater specimens and the corresponding velocity unheated specimens is not good for the zirconium alloys but is good for the stainless steel. The number of these and of heater specimens is small.

d. Heated specimens of all these materials showed several times as much corrosion as unheated specimens at the same velocity. These comparisons are based on average heated values for each material using minimum for stainless and maximum for zirconium alloys.

   The approximate ratios of heated to unheated corrosion for each material are as follows:

316 stainless steel	3.5
Zircaloy-2	5.5
Zircaloy-4	4.2

   Average heat flux for all heated specimens was 75,000 Btu/hr ft^2 and fluid velocity was 10 ft/sec.

2. Cadmium Deposition

The information included in Tables 19, 20, and 26 indicates the following:

a. There is no effect of velocity on the depoisition of cadmium on the 304 and 316 stainless steels, the Zircaloy-2 and the zirconium-niobium alloy. There is an increase in cadmium deposition on zirconium-4 with increasing velocity.

b. There is poor agreement between the deposition on specimens at the ends of the heater and the velocity holder specimens for Zircaloy-4 and stainless steel.

c. There is a very large variation in the cadmium deposited in the heated specimens. This applies to each material and is illustrated in Figures 35, 36 and 37. In each case the deposition rate increases to a maximum in the direction of flow and then decreases near the heater ends. Since the corrosion rates seem to depend on heat flux for all the materials and do not exhibit such variation, it is likely that the heat flux is fairly uniform. An explanation of

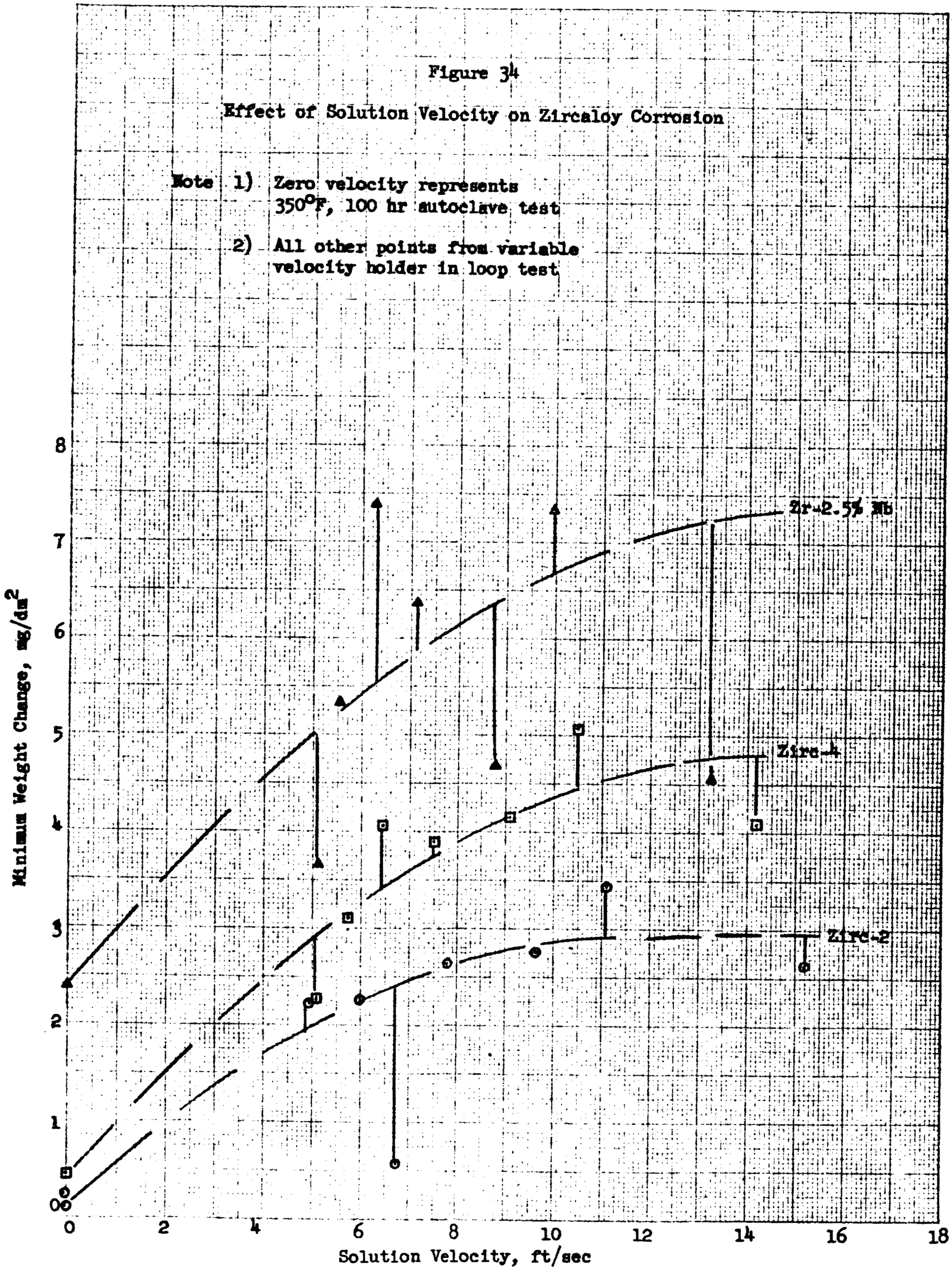


Figure 34
Effect of Solution Velocity on Zircaloy Corrosion
Note 1) Zero velocity represents 350°F, 100 hr autoclave test
2) All other points from variable velocity holder in loop test
Zr-2.5% Nb
Zirc-4
Zirc-2
Minimum Weight Change, mg/dm²
Solution Velocity, ft/sec
0
2
4
6
8
10
12
14
16
18
1
2
3
4
5
6
7
8

Table 26

Comparison of Cadmium Deposition
as a Result of All Types of Tests

	Cadmium Deposition, μg/cm²		
	316 SST	Zr-2	Zr-4
A. Bench Tests 215°F, 100 hours pH = 3-6	<.2 - 1.6	<.2 - 1.2(1)	<.2 - .8
B. Autoclave Tests 350°F, 100 hours pH = 3.4	2.0 - 2.2	<.2 - .5	<.2
400°F, 100 hours pH = 5.88	9.2 - 10.0	.3 - .6	<.2 - .7
C. Loop Tests(2) 350°F, 90 hours pH = 3			
1. Velocity Holder	3.9	0.3	2.9
2. Ends of Heater	0.3	0.2	0.5
3. On Heater Element	3.6	1.3	3.2

(1) Does not include Bench Test #2 data as an uncontrolled lot of material was used.

(2) All values are averages except for Zr-4 velocity holder results which are for 10 ft/sec specimen.

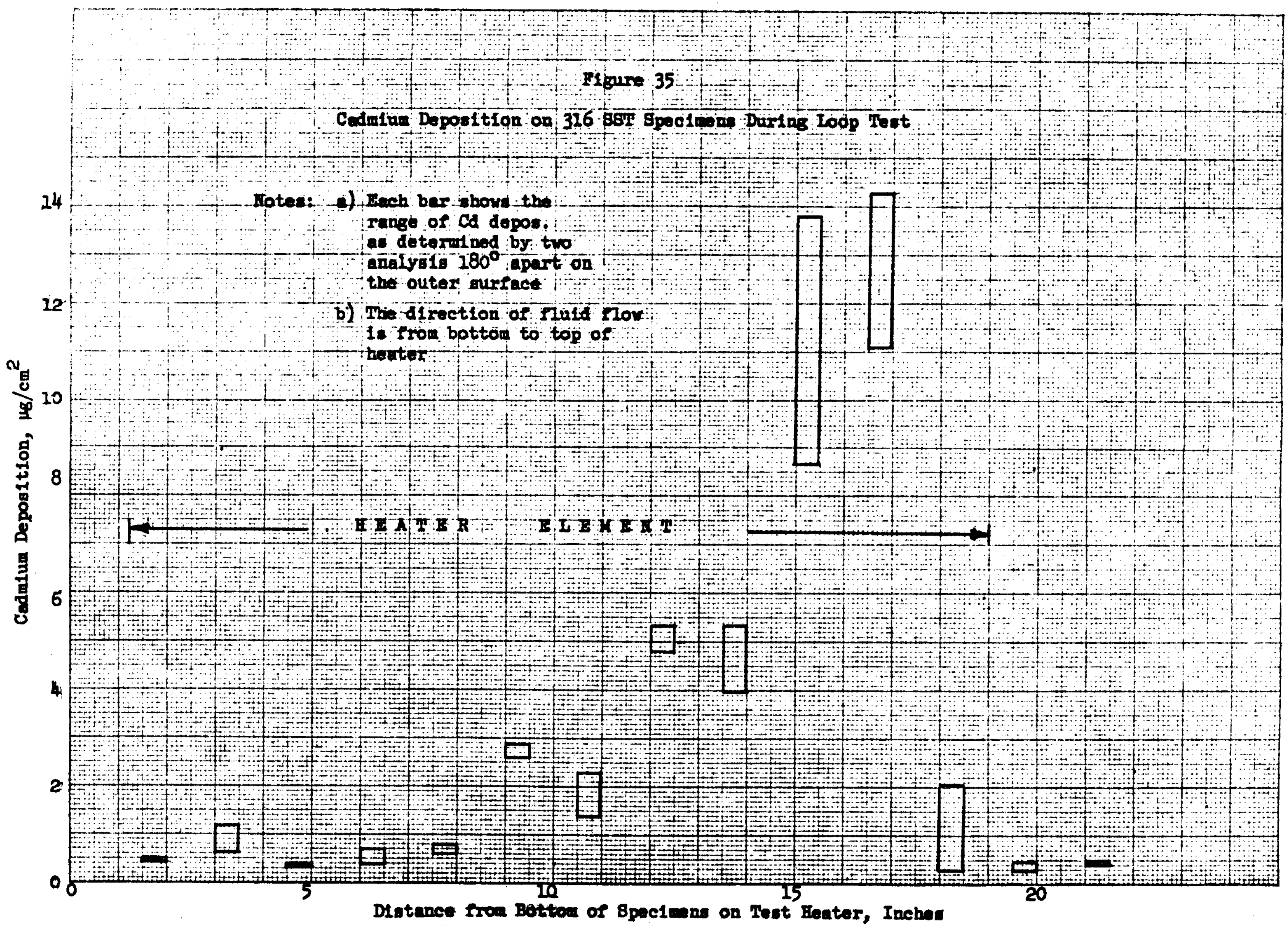


Figure 35

Cadmium Deposition on 316 SST Specimens During Loop Test

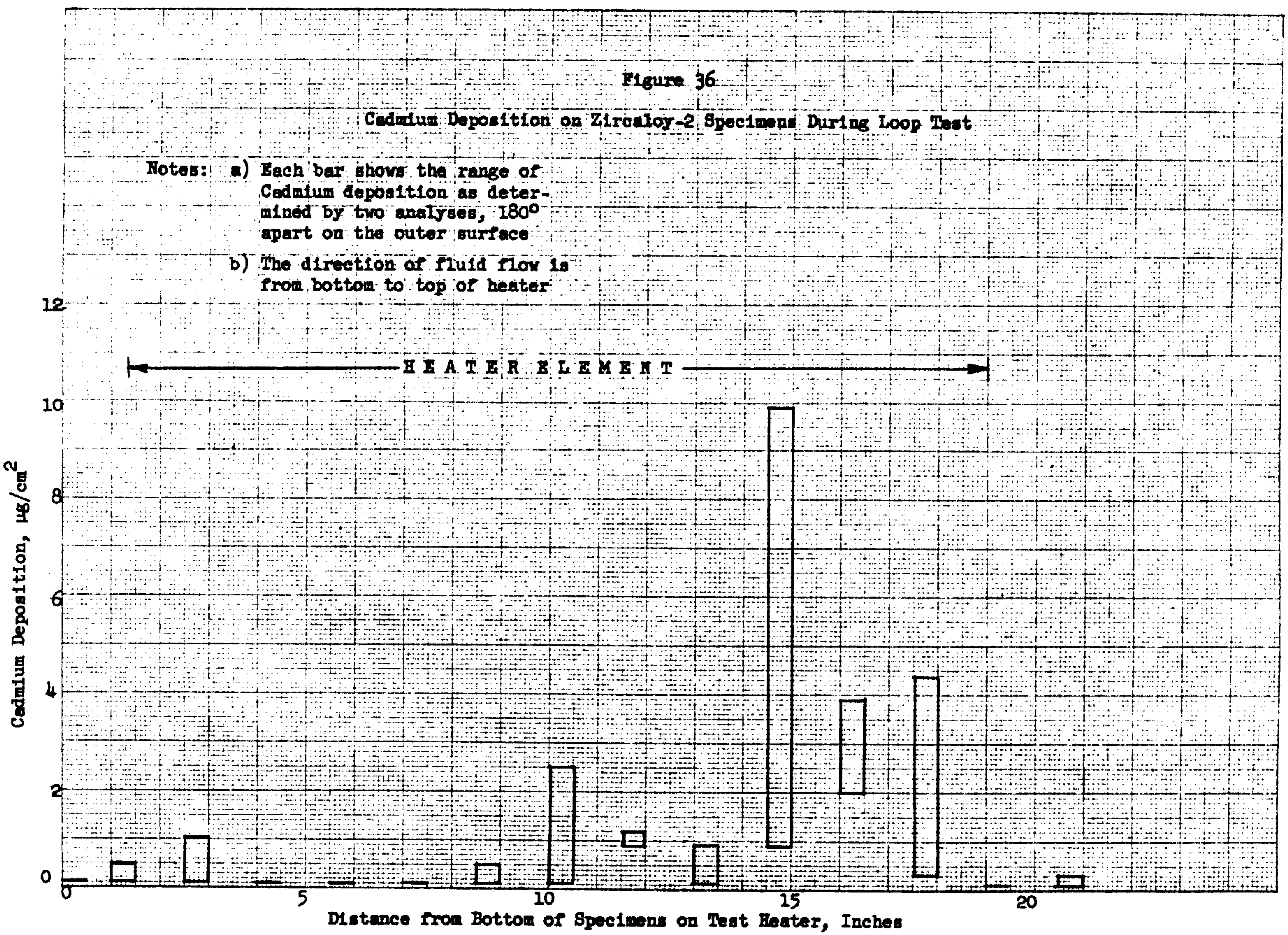
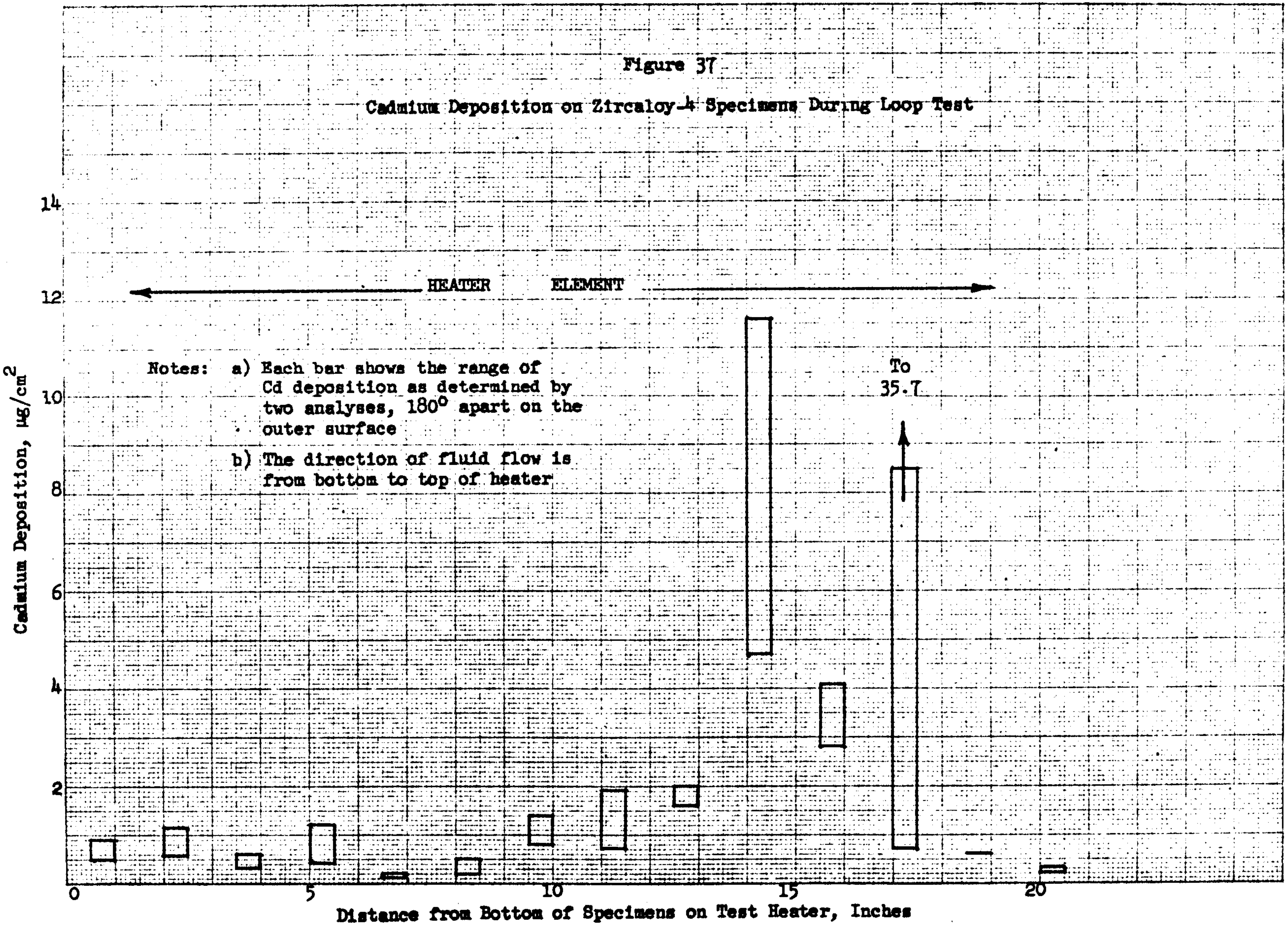


Figure 36

Cadmium Deposition on Zircaloy-2 Specimens During Loop Test

Figure 37

Cadmium Deposition on Zircaloy-4 Specimens During Loop Test



this large variation is not apparent. Some possible reasons are listed below:

(1) Thermal contact between the heater and samples varies circumferentially and a measurement of cadmium deposition at only two locations is giving large errors. Since the corrosion data is based on total weight change, circumferential variation would be averaged out.

(2) Cadmium may be preferentially deposited on the hottest surfaces in contact with a solution with only slight temperature differences being significant.

In any event, the cadmium deposition varies with constant heat flux over a wide range. If the variation is due to measurement techniques only, the values should be averaged to get the effect of the heat flux. Such a procedure indicates that heat flux has no effect on the deposition on 316 stainless steel and Zircaloy-4 and that the deposition is increased by a factor of 4 on Zircaloy-2.

If the observed variation is real and not the result of measurement inaccuracies, some factor other than heat flux by itself is causing the increase in deposition. This is indicated by the fact that many of the samples, as shown in Figures 35, 36 and 37, are experiencing deposition rates no higher than the unheated specimens in the velocity holders.

It is impossible to say which of these two alternatives corresponds to the actual situation. Furthermore, other alternatives are probably possible. Some additional information regarding cadmium deposition was gleaned from the various experiments but do little to clarify the situation:

(1) In the bench tests, most all of the cadmium found out of solution after test, was adhering to the flask walls, through which passed the heat to keep the solutions boiling. The heat flux is estimated to have been about 7,000 Btu/hr ft^2 for about 50% of the test duration if only the bottom area of the flask were used. If the entire area contacted by fluid were used, this flux would drop to about 2,500 Btu/hr ft^2. The amount of cadmium deposited on the glass walls was up to 3 orders of magnitude higher than that deposited on the specimens through

which there was no heat flux. But again, there was a very large variation in the magnitude of the effect for an apparently constant heat flux.

(2) After running autoclave tests 1, 2 and 3, all in the same system, the internals of the autoclave were cleaned by an alkaline permanganate-citrate cleaning method. The citrate solution and the rinse were analyzed for cadmium. The total found was 72.2 mg of cadmium, which does not include any that might have been removed by the permanganate solution. Using the surface area covered by fluid, this amount of cadmium results in a uniform deposition of 52 $\mu gCd/cm^2$. The heat flux is estimated to have been about 5,000 Btu/hr ft^2 for 50% of the 1100 hour test duration. The maximum deposition on the 316 type stainless steel specimens present during these series was 6.7 $\mu g/cm^2$ after the first 500 hours at 400^oF and 3.45 $\mu g/cm^2$ after 500 hours at 350^oF.

(3) The residue found in the pipe containing the loop heater (Residue 9, Table 18) was highly enriched in cadmium and was the largest amount recovered from any single source. This residue was very chunky in nature and many of the pieces had the appearance of having been attached to a curved surface at one time. The loop heater developed a heat flux of 20,000 Btu/hr ft^2 and was on almost continuously for the 90 hour test duration. If it is assumed that all of the cadmium found just under the loop heater was cause to leave the solution at the heater surface, then 4600 μgCd left the solution per cm^2 of heater surface area. The maximum heater surface temperature was calculated to be 400^oF with a fluid velocity of 0.8 ft/sec past the heater.

VIII. REFERENCES

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IX. CONCLUSIONS

The purpose of this study was to establish the relationships between a poison solution, namely cadmium sulfate and various structural materials being considered for use in the CPLS, with respect to the following factors:

1. Solution stability
2. Cadmium deposition
3. Corrosion

This study, employing varying types of tests, each utilized to provide answers regarding some of the many parameters involved, was also expected to provide direction for future programs aimed at determining the ability of a chemical poison loop system to control reactivity of a tungsten-water moderated rocket reactor.

The program and the results obtained, as previously described, fulfilled these requirements; namely to establish the above mentioned relationships where possible, and to define areas requiring further investigation.

The poison solution stability, defined as the apparent loss of cadmium from solution subjected to various test conditions as compared to pretest solution cadmium content, was investigated as a function of:

1. solution temperature
2. solution pH
3. duration of exposure to these conditions
4. influence of metallic surfaces
5. heat flux across solution-metal interface
6. solution velocity

Solution Stability

It can be concluded from the bench or beaker tests that at temperature up to 215°F for periods of time up to 100 hours, solution pH has little effect on solution stability in the absence of metallic surfaces in the pH range of 2 through 7. The loss of cadmium under these conditions is between 0.2 and 0.6% of that initially present. In addition, the presence of Zircaloy-2, Zircaloy-4, Zircaloy-niobium, or inconel, have no effect on this stability under these conditions. The same could be said for 316 and 347 SST up to a pH of 5. However, between 5 and 7, there is an apparent decrease in solution stability. In the presence of 6061-Aluminum, stability is poor at all pH levels.

From examination of autoclave results, it appears that a relationship has been established between temperature and stability as evidenced in Figure 20. Autoclave tests run at temperatures between 250 and 400°F show a decrease in stability with increasing temperature. One must be cautious when comparing these results with 215°F results, where the ratio of surface area of metal to volume of solution is considerably smaller. However, Figure 21 show an apparently decreasing stability with increasing metal to volume ratio. There is apparently little effect of solution pH on stability even at these elevated temperatures. With this assumption, then tests 2 and 3a, run for 100 and 500 hours respectively, show that time of exposure has no effect on stability.

The loop tests were not run primarily to determine solution stability. Their main function was to add information to the cadmium deposition and corrosion pictures and these effects will be discussed later. However, it should be noted that more cadmium was lost from solution than in any of the bench or autoclave tests. The only differences in this test were the heat fluxes from the specimen heater and the loop heater, and the fluid velocity. Since velocity by itself should not have any effect on stability, it remains then that increased heat flux causes decreased stability. The magnitude of this effect is uncertain.

In summary the, solution stability is decreased by increasing temperature, increasing surface area of metal exposed to solution, and increased heat flux; but is unaffected by solution pH.

Cadmium Deposition

The cadmium deposited on 316 SST, the three zirconium alloys and inconel in the bench tests was all below 3 $\mu g/cm^2$ and was unaffected by solution pH. The deposition on 347 SST was substantially higher above pH of 6. Aluminum specimens exhibited considerably greater deposition than any other material at all pH levels.

The 100 hour autoclave test results show that temperatures up to 400^oF have no effect on the deposition of cadmium on Zircaloy as compared to the bench test results. At 400^oF there was a slight increase of deposition with time up to 500 hours. There was no effect of exposure duration at 350^oF.

Both 316 SST and 347 SST behaved quite differently; the deposition increasing considerably with increasing temperature for the 100 hour test comparisons. At 350^oF the deposition also increased with time; whereas at 400^oF it appeared to decrease then increase between 400 hours and 500 hours.

Cadmium deposition is not effected by solution velocity for 316 and 304 SST, Zircaloy-2 and zirconium-niobium alloy as evidenced by the 350^oF autoclave test and the loop specimen in the variable velocity holder and on the end of the test heater. Deposition on Zircaloy-4 seemed to increase with increasing velocity, tripling from 5 to 15 ft/sec fluid velocity.

The effect of heat flux on cadmium deposition on metallic surfaces is not very clear. Some of the specimens on the test heater had very high depositions, but the patterns could not merely be explained as being caused by heat flux. On the other hand, the cadmium deposition and residues found associated with heat flux surfaces from all types of tests; i.e. bench, autoclave and loop tests, all seem to establish a heat flux-deposition relationship. This is one area that will require further investigations before valid conclusions can be made.

Corrosion

Corrosion of structural or containing materials is not only important because of the associated weakening of strength or decrease of integrity. A product of corrosion is hydrogen, and for the TWMR application, its production should be limited or at least predictable.

From a structural integrity view point, corrosion is not a factor under any of the conditions examined for all material except aluminum. The corrosion of aluminum is considerable at all pH levels tested and very severe below a pH of 5.

The production of hydrogen can be predicted using the information presented in previous sections of this report. The factors influencing corrosion, and therefore the hydrogen production are:

1. increased temperatures, increase hydrogen production for all materials tested

2. increased exposure to solution, increases production; the rate of production reaching a steady state value after some period of time

3. increasing fluid velocity, increases production for the zirconium alloys; no similar effect is evident for the stainless steels

4. heat flux had an apparent effect on corrosion, increasing it by factors of 3 to 6. This is clouded by the possible temperature effect caused by forced convection on one side of the specimen as opposed to a situation of something between a stagnant gap and poor metal-metal oxide contact on the other side of the specimen.

X. RECOMMENDATIONS

It is quite evident that further studies will be required before establishing the engineering design of a chemical poison loop system for reactivity control.

In light of the program just completed, it is recommended that:

1. For a system using cadmium sulfate as the poison solution the following programs be undertaken:

    a. a research effort be initiated to determine the compounds present in the test residues. This will help establish the processes by which these compounds are formed

    b. determine the exact relationships existing between stability and deposition, and the factors causing them, with special emphasis on; (1) the effect of temperature

        (2) the effect of heat flux

        (3) the effect of surface to volume ratio

    c. run proof tests duplicating system geometry, materials and operating parameters wherever possible

    d. investigate the use of containing materials other than those considered in this study.

2. An investigation be launched to find a substitute poison solution for cadmium sulfate with emphasis being placed on boric acid solution. The compatibility of boric acid with 316 stainless steel and Zircaloy-2 has been well established in tests at WAPD and in operating reactors. The information still required is the effect on boric acid solution radiolysis at neutron and gamma flux intensities and energy as will be experienced in the CPLS.

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